FLUIDIZED BED ELECTROWINNING OF COPPER

Final Report

July 1997

Work Performed Under Contract No. FC07-92ID13081

For
U.S. Department of Energy
Assistant Secretary for
Energy Efficiency and Renewable Energy
Washington, DC

By
Metalor USA Refining Corporation
North Attleboro, MA

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COOPERATIVE AGREEMENT NO. DE-FC-07-92ID13081

July 1997

Submitted to:

U.S. Department of Energy
Contracts Management Division
Idaho Operations Division
Idaho Falls, Idaho 83402

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I. EXECUTIVE SUMMARY

A fluidized bed electrode consists of a bed of conductive particles fluidized by an upward flow of electrolyte. A metallic conductor is inserted into the bed to provide an electrical connection to the particles. When current flows, the entire bed behaves as an electrode with high surface area. This high surface area leads to two processing strategies: (a) if the current density on individual particles is maintained close to values found in conventional electrolytic processes, the bed will have an extremely high productivity per unit volume; and (b) if the bed is operated at conventional levels of superficial current density (current divided by cross-sectional area of the separator dividing anodic from cathodic electrodes), the bed will operate at nearly equilibrium conditions allowing difficult electrolytic separations to be accomplished.

Fluidized bed electrolysis has been viewed by many investigators as having the potential to significantly lower the capital requirements and energy consumption for electrowinning installations in which metals such as copper, zinc and nickel are recovered from leach solutions. Since these operations consume substantial amounts of energy, small improvements in energy efficiency translate into significant energy savings. However, with few exceptions, fluidized bed electrolysis has remained in the laboratory and has not broken the barrier to the pilot- or commercial-scale. In no situation has a systems approach been adopted in which material handling aspects are addressed in depth.

As part of its precious metals operation, Metalor USA Refining Corporation processes about one ton per day of copper. Several years ago, the company became actively interested in fluidized bed electrolysis as an alternative to conventional electrowinning. As a small copper producer, Metalor USA Refining Corp. must exploit all competitive advantages and it was believed that fluidized bed electrowinning could offer substantial savings in capital and operating costs over conventional cells. Contacts were therefore initiated with the University of California at Berkeley where extensive laboratory testing of fluidized bed electrowinning had been performed. In concert with the Berkeley team, a 1000-amp fluidized bed cell was designed and tested for copper recovery from sulfate solutions. The cell was approximately 10 cm in diameter with a height of about 1 meter and featured the continuous removal of over-size particles. Because of a high length-to-diameter ratio and aggregative fluidization believed to be caused by relatively large particles, regions of poor fluidization developed during electrolysis leading to particle accretions on anode surfaces and dendritic deposition on cathode current feeders, eventually causing short circuits. It was concluded that effective fluidization could be achieved only by using a cell with less wall effect and by utilizing a finer particle size distribution. While the study showed that fluidized bed electrolysis was promising, further work at a larger scale was necessary. The present investigation was therefore undertaken as a collaborative effort with the U.S. Department of Energy.

For this program, a 10,000-amp cell was designed and constructed. The cell, with a circular cross-section, had an internal diameter of about 1 meter and a working height of about 1 meter. The

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important length-to-diameter ratio was substantially smaller than that of the 1000-amp cell built for Phase II. The 10,000-amp cell, constructed of polypropylene covered with fiber-reinforced resin, had twenty six dimensionally stable anodes surrounded by sixty two copper rods serving as cathode current feeders.

Several changes were made in the design of the large cell compared to the smaller Phase II unit to prevent the formation of particle accretions that had severely limited Phase II experiments. First and most importantly, bed diameter was increased relative to bed height to minimize wall effects. Second, the particle size distribution was made substantially finer to promote smooth fluidization over bubbling fluidization. Third, the distributor plate was changed from a conical design to a flat design to minimize pressure differentials across its surface. Also the distributor plate was built with conical holes to eliminate horizontal surfaces onto which large particles could settle.

A central objective of this research was to investigate the continuous removal of product from the large fluidized bed. The bed was designed so that particles of all sizes would be continuously withdrawn from the bed (from a discharge point on the periphery of the base) and recycled to a screen. Large particles were retained on the screen while small particles and solution passed through the screen and were returned to the bed. This was successfully accomplished using an eductor to extract particles from the bed.

Long-term electrochemical experiments were not possible however. In spite of the changes made to prevent the formation of particle clusters, accretions developed within the fluidized bed that led to short circuiting. It is believed that this was due to ineffective transfer of charge from the current feeders to particles in the fluidized cathode. High current densities at the current feeders resulted in dendritic growths that hindered fluidization. Particles became trapped near the dendrites, forming clusters that eventually short circuited the cell. Moreover, the use of smaller particles enhanced the dissolution of copper into warm sulfuric acid solutions and overall current efficiencies were substantially lower than those achieved in Phase II. (However, current efficiency should not be the measure of success in this type of program; relatively high current efficiencies could be obtained in the early stages of an experiment.) Experiments ultimately had to be curtailed because copper deposited in such a way as to short circuit the cell.

To promote current flow into the bed, another strategy evolved. The relatively fine copper particles (with a mean size of about 0.2 mm) were replaced with larger graphite particles (with a mean size of about 2 mm). Graphite was selected to allow visual monitoring of deposition in the cell. Instead of operating at a bed expansion of about 20%, sufficient flow was provided to barely fluidize the particles. At intervals of about 30 minutes, the bed was expanded to over 60% to allow mixing to occur. In some experiments, the spacing between anodes and cathode current feeders was increased to promote this mixing.

Under these conditions, deposition occurred much closer to the anodes, as expected from prior investigations. Particles near the cathode current feeders, while coated with copper, were not

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welded together as had been found in experiments with copper particles. Near the membranes, however, microdendrites formed making it difficult to "clean" the membrane surfaces during mixing intervals. Given sufficient time, deposits would traverse the membrane and cause small-scale short circuits. While current efficiencies were relatively high for the initial period of an experiment (the first eight hours or so), current efficiency would drop to zero as the shorts became pervasive. To prevent this, an additional spacing was provided between the anode and the membrane and anodes were filled with dilute sulfuric acid electrolyte before testing. Even with the additional space, short circuits eventually formed preventing copper deposition through electrolysis.

The idea of intermittently fluidizing a fixed bed electrode is worthy of further investigation. However, it is believed that the concept of a fluidized bed electrowinning cannot be considered to be viable for industrial electrowinning operations in which copper is recovered from sulfuric acid electrolytes. The requirements for adequate spacing and uniform bed density directly contradict the need for small spacing and good particle contact to overcome the dissolution reaction. Particles must be suspended in solution to prevent particle clusters from forming. But particles must remain in close contact to allow for charge transfer and deposition. The conditions that lead to uniform bed density (fine particles, large spacing, high solution flowrates) also promote dissolution. An operating regime could not be found wherein these two opposing requirements could be balanced. An intermittently fluidized bed represents a compromise between these opposing factors. Further work is required if such a hybrid can be considered to be viable or whether attention should be focused on alternatives to fluidized beds.

II. ACKNOWLEDGMENTS

III. INTRODUCTION

A. Fluidized Bed Technology

When a fluid flows upwards through a packed bed of fine particles, the behavior of the system changes as the velocity increases. At low flow rates, the fluid percolates through the particles without moving the particles. As fluid velocity increases, pressure drop through the bed increases but particles retain their positions with respect to their neighbors. This is called a fixed bed. At some point, known as the minimum fluidization velocity, the frictional force between the particles and the fluid equals the weight of the bed. Velocities above the minimum fluidization velocity cause the bed to expand into what is referred to as a fluidized bed. In contrast to fixed beds, a fluidized bed is characterized by substantial motion of particles relative to each other. At small multiples of the minimum fluidization velocity, the bed expands smoothly in a condition of smooth or homogeneous fluidization. Beyond this point, bubbles of liquid free of particles begin to form within the bed and rise upwards resulting in aggregative or heterogeneous fluidization. The bubbles have two consequences: (a) further expansion of the bed does not occur and (b) fluid in the bubbles does not contact particles preventing interaction between the two phases. Further increases in flow velocity cause physical entrainment of small particles. At sufficiently high velocities, all particles are carried out the bed by the fluid.

There are numerous advantages to fluidized beds:

- Excellent particle mixing leading to good temperature control and uniformity. This attribute has been used in numerous applications for treating heat-sensitive materials.

- Excellent mass transfer between the fluid and particles. This is the basis of many catalytic, combustion or calcination reactions utilizing fluidized bed reactors.

- Excellent heat transfer between the fluid and particles and the walls and internals of the reactor. Many applications rely on direct heat exchange between the fluid and solids or indirect heat exchange between the bed and an immersed heat-transfer surface. Examples are fluidized bed boilers and coolers.

- Material handling is simpler in fluidized beds than in fixed beds because the particle/liquid mass behaves like a fluid.

The disadvantages of fluidized beds are a consequence of the excellent mixing within the bed and its aggregative behavior at higher flow rates. These are:

- Particles display a wide distribution of retention times. As a result, multi-stage operations are necessary for applications where a narrow range of retention times is needed.

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- Bypassing of fluid in bubbles or slugs leads to inefficient contacting between solids and liquid. This requires a trade-off between more efficient particle mixing achievable at higher velocities and the decreased fluid bypassing found at low velocities.

Fluidized bed technology has been is use for about 70 years. The first application of a fluidized bed was in the Winkler process, commercialized in 1926. This process gasified low-rank coals in a shallow fluidized bed to produce a mixture of hydrogen and carbon monoxide gases. During World War II, catalytic cracking of petroleum and the generation of carbon-coated cracking catalyst was successfully performed in fluidized bed reactors. Since then, most commercial applications have involved gas fluidization; examples include high-temperature roasting of sulfide minerals, reduction of iron ore, calcination of limestone and cement clinker and a wide variety of catalytic, coking and combustion reactions in the petroleum and petrochemical industries. Liquid fluidized beds have been used for biochemical reactions and the growth of cell cultures.

B. Fluidized Bed Electrodes

A fluidized bed electrode consists of a mass of conductive particles fluidized by an upward flow of electrolyte into which a metallic electrode is inserted to provide an electrical connection. Originally, it was believed that charge transfer occurred via particle-to-particle collisions resulting in a sharing of charge. Subsequent work has shown that charge transfer is through the formation of temporary chains extending into the bed from the metallic electrodes. Either a cathode or an anode (or both) can be fluidized electrodes and several geometries are possible for the spatial relationship between anodes and cathodes. The most common, and the one adopted in all work at Metalor USA Refining Corporation, is the side-by-side configuration in which the cathode and anode compartment must necessarily be separated by a porous membrane.

A side-by-side configuration for a fluid bed electrode is geometrically similar to the traditional electrowinning cell with planar electrodes. The important measure of the intensity of cell operation is current flow per unit area of the separator between the electrodes. This is called the superficial current density. In a fluidized bed electrode, the actual current density (the current density per unit area of particles in the electroactive mass) is usually much lower than the superficial current density.

Two strategies have developed for operating a fluidized bed electrode based on the superficial current density. If the superficial current density is kept at the same level as that used in conventional planar electrodes (on the order of 200 to 300 amps/m^2), the actual current density is low and the electrode operates close to equilibrium. This approach is suited for recovering low concentrations of metals from dilute streams such as waste water. The other operating mode is to maintain actual current densities at the level used in conventional cells. This results in high superficial current densities and high productivity and was selected for investigation here.

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C. Economic Benefits of Fluidized Bed Electrowinning of Copper

Adoption of fluidized bed electrowinning by the copper industry has a number of potential economic benefits. While it is not an objective here to quantify these benefits (indeed, until further engineering data are available through studies such as this one, it is not possible to make accurate assessments of some of the economic benefits), it is important to understand the types of benefits that could result from the application of this technology to the extractive metals industry.

1. Reduction in Capital Investment: Standard electrowinning systems with planar electrodes operate at 200 to 300 amps/m^2 of surface area. This translates into a process intensity of 30 to 60 kg copper per day per m^3 of cell volume or 40 to 100 kg per day per m^2 of cell area (footprint). In contrast, fluidized bed cells have process intensities of 1000 to 1200 kg per day per m^3 of cell volume or 300 to 500 kg per day per m^2 of footprint. A typical electrowinning plant producing 25,000 ton per year conventionally requires approximately 600 m^2 of process building. A fluidized bed electrowinning plant would require 25% as much floorspace.

2. Reduction in Energy Consumption: Much of the energy consumed in electrowinning is associated with the nucleation and generation of gaseous oxygen bubbles at the anode and, to reduce this consumption, several investigators have tested alternate anode reactions that do not involve oxygen. While these studies have demonstrated energy savings are possible, none of the proposed reactions have been commercialized. A principle reason for this lack of acceptance by the industry is the difficulty in separating electrode compartments. Since a separator is required in fluidized bed cells, it is natural to consider alternate reactions in such devices.

3. Reduction in Labor Costs: Conventional copper electrowinning is labor intensive because cathodes have to be stripped. One of two approaches is used. In the more traditional approach, starting sheets of copper are deposited on stainless steel blanks for a 24-hour period and then manually stripped. These starting sheets are attached to hanger bars and placed in commercial cells for seven to ten days to achieve final dimensions before being washed and melted. In the more modern approach, stainless steel or titanium cathode blanks are placed directly in commercial cells and the copper deposit is stripped from these blanks. Stripping can be done manually or automatically. The cost of automation is one of the principal reasons why copper electrorefineries have a minimum economic size of over 200,000 tons per year. For a typical electrowinning plant, such automation is not economically feasible.

In fluidized bed cells, copper deposits on a mass of fluidized particles causing particle growth. Large particles are harvested by size separation and are rinsed and melted (or sold as a value-added product). No stripping is required.

4. Reduction in Acid Mist: Acid mist continues to be one of the most pressing problems for electrowinning operations. This mist is formed when small oxygen bubbles break at the cell surface, creating aerosols of electrolyte. New OSHA regulations target the reduction of acid mist

to provide a healthier environment for workers. Attempts to curtail mist formation include polypropylene cell covers, foaming agents, increased local exhaust and, most recently, integral shields attached permanently to anodes.

Fluidized bed cells are intrinsically closed devices. Since there is no need to open the top of the unit to harvest product, the cells can be designed to contain all vapors. The problem of acid mists can therefore be treated with local ventilation in a closed system, a much more manageable situation than trying to ventilate the large open area found over conventional cells. (Replacing the oxygen reaction at the anode also overcomes this problem.)

5. Applicability to Other Systems: The extractive technology of other base metals, notably nickel and zinc, is similar to that of copper. The benefits of fluidized bed technology discussed above apply to these systems as well.

D. Review of Prior Work

1. Fluidized Bed Electrolysis: Pioneering work was done in developing fluidized bed electrodes in the U.K. in the 1960's. This work, performed at the Universities of Newcastle-upon-Tyne and Southhampton, resulted in a National Research and Development Corp. patent in 1970[1] and an attempt was made at piloting the process for copper electrowinning at Constructors John Brown (later CJB Developments Ltd).[2] Commercialization was not achieved because of three major problems: (a) excessive voltage (later shown to be due to a large and unnecessary spacing between anodes and the separating diaphragm); (b) adhesion of the particles to the current feeders (believed to be a consequence of low bed density caused by improper fluidization); and (c) plating and penetration of the diaphragm separating the cathode compartment from the anode (the result of localized areas of high bed density caused by poor fluidization). Attempts to deal with the adhesion problems by imposing circulating patterns in the fluidized bed electrode were not successful. Subsequently, Akzo[3,4] developed a fluidized bed electrode for the removal of metals from dilute wastewater solutions. Several of these early cells are believed to still be in operation in European plants but the process has not been commercialized outside of the company.[5]

In the 1970's, research into fluidized bed electrodes in the U.K. continued at the university level as indicated by a series of patents assigned to NRDC.[6] These patents, with strong academic roots, address processes operated strictly in the laboratory rather than in an industrial setting. Other investigators were also experimenting with fluidized bed electrowinning on a laboratory scale. While much of the work was devoted to copper electrowinning, zinc[7-9], nickel[10], cobalt[11], silver[12] and cadmium[13] were also investigated. (A comprehensive review of investigations into fluidized bed electrowinning is available.[14])

Starting in the late 1970's, a team of researchers at the University of California, Berkeley, started a series of investigations that made significant contributions to fluidized bed electrolysis. In early work[15], a mathematical model was developed and compared with experimental results of copper

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electrowinning in a 100-amp laboratory cell. Superficial current densities of 200 to 600 amps/ft^2 were studied. High current efficiencies were obtained at high current densities with elevated copper concentrations in the electrolyte and in the absence of other reducible species such as ferric ions. This work showed the importance of bed density in controlling the bed resistance to maximize deposition of metal on fluidized particles. At high bed densities (low bed resistance), deposition occurred at the "surface" of the cathode facing the anode, namely the diaphragm. At low bed densities (high bed resistance), deposition occurred on current feeders. Operating conditions delineating these regimes were described by the Berkeley team. Subsequent work[14,16] showed that energy consumption could be reduced through modifications on the anode side by providing a path for oxygen bubbles to escape and, more importantly, by installing the cell separator directly onto an open-mesh anode, thereby reducing the distance between anode and cathode. Several types of separators were tested and the most effective was found to be a microporous membrane produced by W.R. Grace for the automotive battery industry under the trade name Daramic.

The team at Berkeley also investigated alternate anode reactions to avoid the energy penalty associated with oxygen generation.[17,18] The oxidation of sulfur dioxide or sulfite ions was studied since these reactions generate sulfuric acid needed for leaching. Probes were used to measure particle and cell potentials for comparison with theoretical calculations.[19] This work showed strong evidence of bubble formation in the bed. The observations were consistent with a calculated mean bubble diameter of about 15 mm. There was evidence for the absence of bubbles near the bottom of the bed, suggesting that smaller bubbles coalesced as they traveled upwards from the distributor plate.

2. Prior Research by Metalor USA Refining Corp.: The work conducted at the University of California was regarded by Metalor USA Refining Corp. as a Phase I effort to explore fluidized bed electrowinning on a laboratory scale. The research at Berkeley had shown that:

- Cell voltage drops could be significantly reduced by placing the anode directly on the separator;
- The bed resistance is related in a quantifiable manner to bed density; and
- Operating conditions in the fluidized cell could be varied between the extremes of deposition on the current feeders or near the membrane.

It was felt, however, that the 1000-amp cell designed and operated at Berkeley did not provide satisfactory scale-up data because of its relatively thin rectangular cross-section. It was believed that further research was needed on a more equiaxed cell. In addition, experiments had not been conducted over sufficiently long periods of time to demonstrate whether all particles grew uniformly or whether a particle size disappeared through selective growth or dissolution. (Extinction of a particular particle size often occurs with gas/solid fluidized beds.) Information on shifts in the particle size distribution over time would be necessary to evaluate the long-term operability of a fluidized bed system.

More fundamental, however, was that no investigation to date on fluidized bed electrodes (including the work at Berkeley) had considered the possibility of continuous product removal. The prevailing approach had been to consider fluidized beds as batch reactors in which particles could be grown for predetermined operating times after which the cell would be emptied and particles separated based on size. Small particles along with a certain amount of seed particles would be returned to the bed for further processing while large particles, after rinsing, would be considered product. The flaw in this approach is that fluidized beds are inherently continuous devices. Most problems with fluidized beds occur during start-up or shut-down periods. Moreover, without automated materials handling schemes revolving around continuous product removal, the process would not be attractive to industry.

The objective of the Metalor Phase II experimental program was to test a fluidized bed system with continuous removal of oversize particles. The size of the cell was selected to be 1000 amps. This appeared to be a reasonable scale-up from the 100-amp cell used at Berkeley for electrochemical testing yet would give meaningful data for the 10 K-amp cell anticipated in Phase III. A circular cross-section was chosen over the rectangular cell used at Berkeley at the 1000-amp level to aid in scale up and to simplify continuous particle removal.

Figure 1 gives a schematic of the design. The cell body was constructed of transparent polyvinylchloride (PVC) with an internal diameter of 16 cm. The cylinder height was 70 cm. Flanges were welded at both ends to connect the body with the overflow portion on the top and the feed section at the bottom. The bottom portion had a conical distributor plate (angled at 30° from the horizontal) sandwiched between the cell body and a feed plenum. Catholyte was pumped into the feed plenum and flowed upwards through the distributor plate into the cell body, fluidizing the copper particles that constituted the cathode. Simultaneously there was an internal flow of particles downwards through the middle of the conical distributor plate, past a control valve and into a recycle stream. The flowrate of particles in this stream was adjusted by a control valve.

The distributor plate was initially constructed of fiberglass-reinforced plastic. However, the first few experiments quickly showed that the plastic could not survive repeated dismantling and a stainless steel distributor plate was constructed. This plate had an angle of 30 degrees, with 183 holes, each 1.37 mm in diameter. The holes were tapered to allow entrapped particles to be easily removed.

Electrical connections were made at the top of the cell. The dimensionally stable anodes, 1.6 inch in diameter and encased in Daramic membrane, were suspended from the top into the cell along with cathode current feeders. Anodes were filled with electrolyte before testing. Three anodes, separated by a triangular current feeder were used initially, as shown in Figure 2. Two other electrode configurations were also studied. Figure 3 gives a schematic of solution flow through the system. From a holding tank, catholyte was pumped into the fluidized bed cell, through the

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DISENGAGEMENT
ZONE

7.6

29.2

WORKING
ZONE

15.9

71.1

FEED PLENUM

11.4

2.2

RECYCLE
DISCHARGE
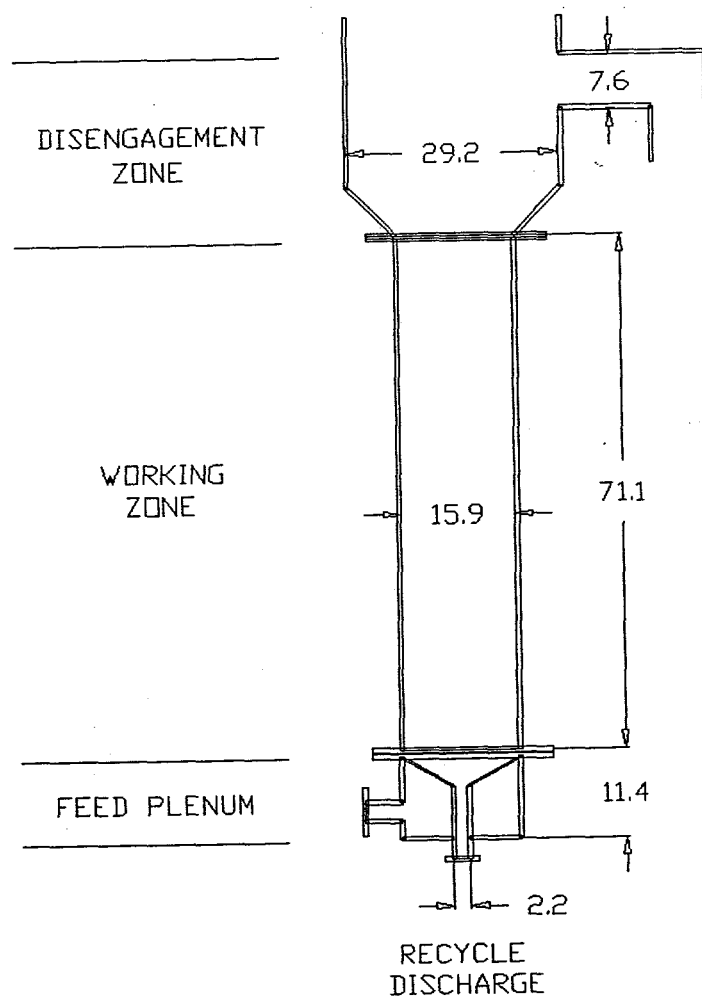
DIMENSIONS IN CENTIMETERS

Figure 1. Schematic diagram of Phase II fluidized bed cell.

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CATHODE
CURRENT FEEDER

ANODE

ARRANGEMENT A

CATHODE
CURRENT FEEDER

ANODE

ARRANGEMENT B

CATHODE
CURRENT FEEDER

ANODE
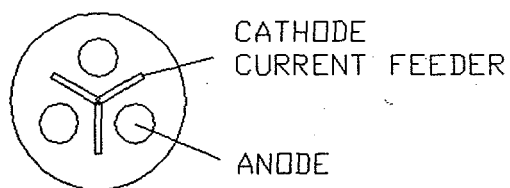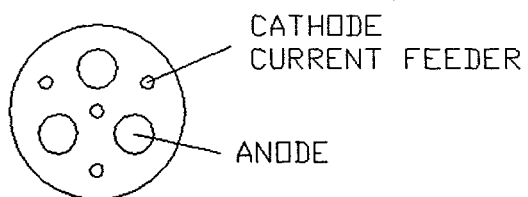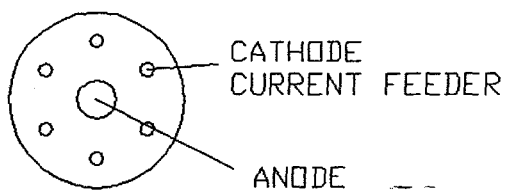
ARRANGEMENT C

Figure 2. Electrode arrangements in Phase II fluidized bed experiments.

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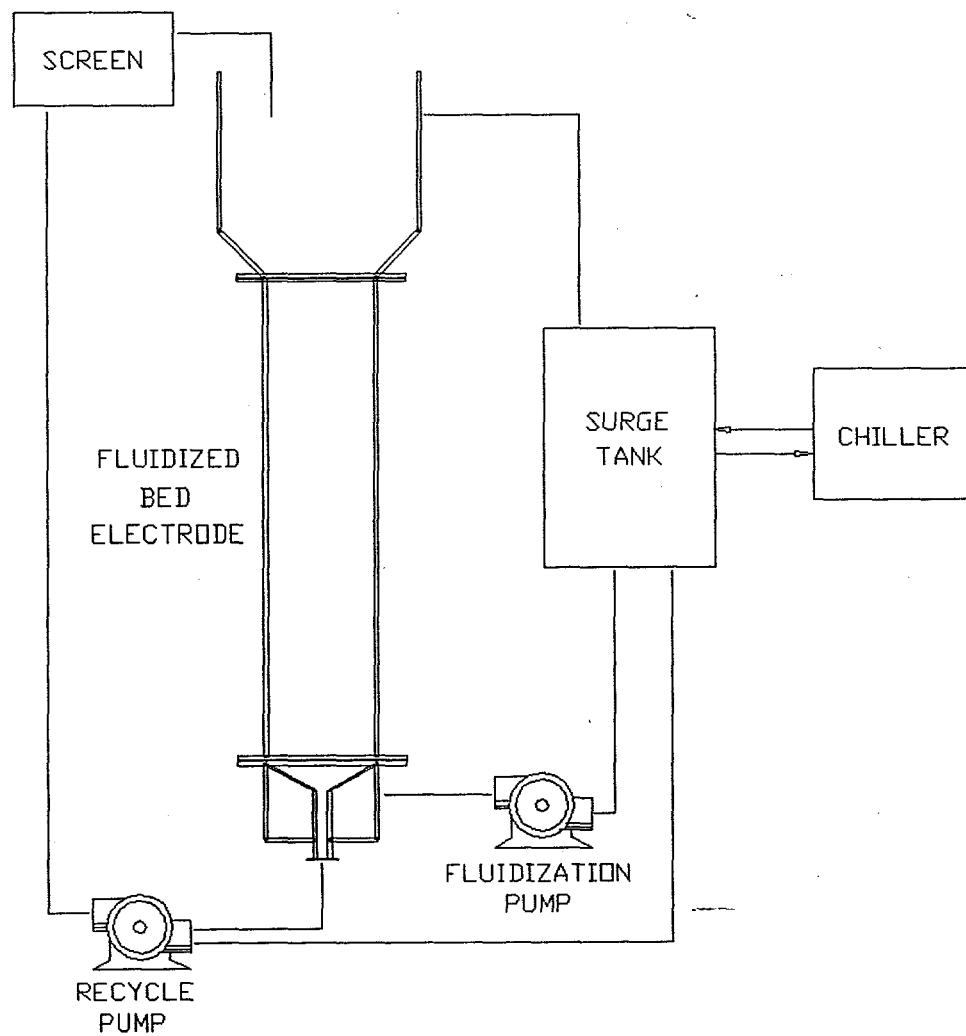
Figure 3. Flow system for Phase II fluidized bed experiments.

distributor plate and flowed upwards to the overflow section where (because of the larger internal diameter), solution velocity was lower and particle disengagement occurred. Solution then flowed by gravity back into the holding tank. At the same time, a second pump recirculated solution past the recycle tee, into which a small stream of particles from the bed flowed. Particles were entrained in the flow and carried upwards to a screen mounted above the cell. Small particles and solution passed through the screen and fell by gravity back into the cell. Large particles were trapped on the screen.

The materials handling aspects of the system were tested with water before experimenting with acid electrolytes. In the material handling experiments, 59 kg of copper shot were added to the cell. (The particle size distribution for copper shot used in Phase II fluidized bed experiments is given in Table 1.)

Table 1. Particle Size Distribution for Phase II Fluidized Bed Experiments.

Size Mesh	Size microns	Weight Percent in Interval
10 to 20	850 to 2000	45 to 55
20 to 30	600 to 850	12 to 15
30 to 40	425 to 600	10 to 12
40 to 50	300 to 425	18 to 33

Several pumping rates were used, corresponding to bed expansions (measured as the relative increase in bed height compared with bed height at no flow) between 10 and 30%.

Simultaneously, the recycle stream was tested. With the recycle pump delivering its maximum flow of 23 l/min, the discharge valve from the fluidized bed was slowly opened. At a certain point, particles began slowly falling through the valve and into the tee to be carried up to the screen. Opening the valve further increased the flow of solids until a point was reached at which the tee became clogged. Clogging was cleared fairly easily by closing the control valve and allowing the tee to empty. Under stable conditions, flowrates of 0.59 to 1.59 kg/min of solids could be recirculated, corresponding to mean residence times in the fluidized cathode of about 40 to 100 minutes.

Large particles were then added to the bed to determine time required for complete collection. Silver grain, in the range of 8 to 14 mesh, was used because its color contrasted with the copper particles. Once the silver particles were added to the bed, they could occasionally be seen at the side walls passing slowly downwards to the bottom. Complete recovery taking over two hours.

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The fact that all silver particles did not appear in the screen at the same time was indicative of the high degree of mixing that could be obtained in the fluidized cathode.

The fluidized bed was repeatedly started up and shut down to determine the conditions causing particles to fall through the distributor plate to the feed plenum. It was found that the bed could be shut down without excessive particle loss as long as it was not drained of solution. The action of the liquid flowing downwards through the distributor plate caused some particles to be displaced. It was also found that the bed could be emptied fairly quickly using the recycle stream if the flow of fine particles (screen undersize) was redirected from the screen to another container. Only a small fraction of the original charge could not be removed in this manner.

The most serious problem occurred when bubbles of air became entrained in the flow. The hydrophobic nature of the copper particles meant that air bubbles were very effective in transporting copper particles to the surface of the overflow and from there into the surge tank. This problem was eliminated by properly positioning the overflow line in the surge tank to prevent air entrapment and the subsequent creation of bubbles.

Following the successful materials handling experiments, electrochemical experiments were initiated. Electrochemical investigations usually measure the effect of operating variables (current density, bed expansion, etc.) on overall efficiency measured by energy consumption per unit of product. For a new type of electrochemical reactor, however, these measurements are not sufficient to assess the feasibility of the technology. Laboratory programs can demonstrate that a device is electrochemically efficient and such experiments have been carried out by many investigators on fluidized bed cells. But scaling up from the laboratory to the production arena opens up the question of operability that must be addressed in pilot plant testing. Operability issues were central to the Phase II program conducted by Metalor USA Refining Corporation on fluidized bed electrowinning.

Electrochemical experiments dealt with the electrowinning of copper from sulfuric acid solutions in which the cathode reaction for the recovery of copper:

$$Cu^{+2} + 2e^- = Cu^0$$
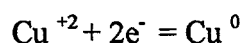
was coupled with the oxidation of water to form oxygen:

$$H_2O = 1/2 \, O_2(g) + 2H^+ + 2e^-$$
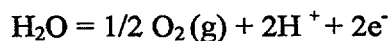
Besides the reduction of copper on fluidized copper particles, the secondary reaction of hydrogen formation occurred. (Hydrogen bubbles could be observed forming at copper surfaces at low dissolved copper concentrations.)

Solutions contained variable concentrations of copper and free acid but none of the other common impurities found in conventional electrowinning solutions. Since the cell was not operated as part of a leach/electrowin circuit, copper concentrations dropped as electrowinning experiments progressed. During these experiments, catholyte copper concentrations varied from 30 g/l to less than 100 ppm and free acid concentrations ranged from 50 to 110 g/l. Anolyte, though separate from catholyte because of the membrane, was initially at the same composition; the anodes were simply filled with copper sulfate solution before starting an electrowinning experiment. The solution level inside the anodes was checked periodically and adjusted as necessary.

Standard procedure was to operate the bed under a given set of operating conditions (percent fluidization, recycle flowrate, amperage) for about eight hours, or until an obvious problem developed. Actual test durations ranged from 4 to 8 hours. Electrolyte samples were taken at regular intervals to monitor the progress of the experiment by changes in copper and free acid concentrations. At the end of an experiment, power was shut off and the bed emptied. Anode tubes and cathode current feeders were removed from the bed for visual inspection and, if necessary, the distributor plate was disassembled for cleaning. If particle deposits were found on the electrodes, a new set of conditions was specified for the next experiment. If after adjusting the current density and bed expansion, unsatisfactory deposition on the membrane or current feeders was found, the arrangement of the electrodes inside within the bed was modified and a new set of exploratory experiments begun. Over forty experiments were conducted in this manner.

Table 2 summarizes experimental conditions and results for these experiments. The first nine experiments dealt with solution flow and particle fluidization. Recycle flows of both solution and particles were measured. Of particular note was Experiment 6 in which silver particles were added to the bed. As discussed earlier, because of the color difference, the behavior of the silver particles could be monitored visually through the Plexiglas side walls and the rate of appearance of the silver particles in the recycle stream was measured. It was found that these particles, though higher in density than the copper particles, were well mixed in the bed and did not segregate to the bottom of the unit. Several hours were required to recover all the silver particles from the flowing recycle stream by collection on the recycle screen.

With rare exceptions, current efficiencies for the electrochemical experiments were positive, some as high as 70%. However, the copper that did deposit did not appear to plate uniformly throughout the fluidized cathode. The principal difficulty encountered in these experiments was the growth of particle accretions at various points within the fluidized cathode caused by regions of poor fluidization. As the formations grew, flow velocities were further impaired causing further growth and eventually resulting in a short circuit. Usually the formations were found on anodes, but under conditions of high bed expansion, deposits formed on the cathode current feeders. In many experiments, the recycle stream was shut off to insure that secondary flows were not interfering with uniform fluidization within the bed.

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Table 2. Summary of Phase II Fluidized Bed Experiments.

Test	Bed Expansion (%)	Duration (hr)	Current (amp)	Cell Voltage (volt)	Current Efficiency (%)	Comments
1						Water testing; initial charge of copper particles; measured recycle flow
2						Water testing after modifications - increased overflow area, cleaned distributor
3						Test of chiller to control temperature; reached low of 7° C
4						Bulk density measurements
5						Water testing with copper particles and cooling; constant fluidization for 7 hr
6						Added silver grain to bed (1.2 x 2.4 mm); recovered 80% in 2 hr
7						Measurement of copper passing through distributor plate
8						Shut down bed with copper particles in place; restarted without difficulties
9						Replaced fiberglass distributor plate with stainless plate
10		2	450	5.2	45	Shutdown because current feeders overheating
11	25	2.5	340	5.2	60	Possible short near end of test
12	15	2.5	400	3.2	60	Deposition near top of anodes
13	30	2.5	400	3.2	32	
14	35	2.5	400	3		Deposition on membrane
15	34	5		3		Copper buildup on cathodes
16	32	2	120	3	98	
17			150	4		First run with Type B electrode arrangement
18		5	100	2.4	138	
19	27	7	300	3	27	
20	28	2.75	400	4	16	
21	20	3.5				First test with Type C electrode arrangement
22		4	100	5.8	92	
23						Added larger copper particles to bed; particles segregated based on size
24	18	2.5	200	5		Changed particle size distribution; no segregation observed
25		3	200	4.5		
26		1.5				
27		1	—			
28		6				
29		7				
30	20	4	200	5	58	Double membrane wrap on anodes
31	18	3	100	5.2	59	
32		4.5	200		73	
33		5	0			Dissolution test; operated without power
34		7				Test of different means of distributing power over anode surface
35						
36	18	6				
37	18	6	200	4 to 5		
38	18	8				
39						Tests of various holes in distributor plate for finer copper powders
40						Fluidization tests with finer copper particles
41						Membrane tests

Three different electrode arrangements, shown in Figure 2, were tested. The design evolved from a relatively closed arrangement with a single "Y"-shaped current feeder surrounded by three anodes (Arrangement A), to replacing the solid "Y"-shaped current feeder with four cylindrical current feeders (Arrangement B), to a single anode surrounded by six current feeders(Arrangement C). Arrangement A was used for the first 17 experiments, Arrangement B for the next five and Arrangement C for the remaining experiments. The driving force for this evolution was the need remove restrictions in the cathode that were contributing to poor fluidization and causing particles to form solid clusters within the bed. In all cases, however, these accretions were found within the cathode if experiments were continued for a sufficient time.

Figures 4 and 5 present data from two typical experiments showing the drop in copper concentration with time. Data are given for two of the electrode arrangements studied, Figure 4 for Arrangement B and Figure 5 for Arrangement C. Current efficiencies for the two experiments are 27% and 57% respectively. These values are representative of the results obtained in the Phase II investigation.

Current efficiencies did not approach 100% in these experiments as is common with most conventional electrowinning systems because of the constant dissolution of copper in the warm, oxygenated sulfate solutions. In one experiment, Experiment 33, the cell was actually operated for an extended period without power so that the rate of dissolution could be measured. Overcoming this dissolution required that a minimum current be applied to the cell. As the electrode system evolved, more electrodes were removed, requiring lower currents and resulting in poorer efficiencies. The requirement for sufficient space between the electrodes to allow for acceptable fluidization conflicted with the need for tight spacing to maintain cathodic potentials on the particles. As early as 1970, Hiddleson and Douglas[20] showed that particles 1 cm or more from the cathode current feeders were at the same potential as the electrolyte. Sabacky and Evans[15] estimated this distance at between 1 and 3 cm depending on operating conditions (solution conductivity, bed density, etc.) As our spacing increased to accommodate better fluidization, more particles were subjected to dissolution, thereby lowering overall efficiency.

It was concluded that the 16-cm diameter bed was too small relative to the diameter of the anodes and current feeders. Wall effects were already significant given a 4:1 length to diameter ratio. The combination of these effects and the relatively small distances between electrodes resulted in areas of poor fluidization within the bed in which particle clusters developed. Short circuits, combined with conditions conducive to dissolution (high mass transfer rates, elevated temperatures, high dissolved oxygen content), detracted from overall current efficiencies. Leaks of oxygenated anolyte into the cathode compartment impaired current efficiency by promoting dissolution of copper particles.

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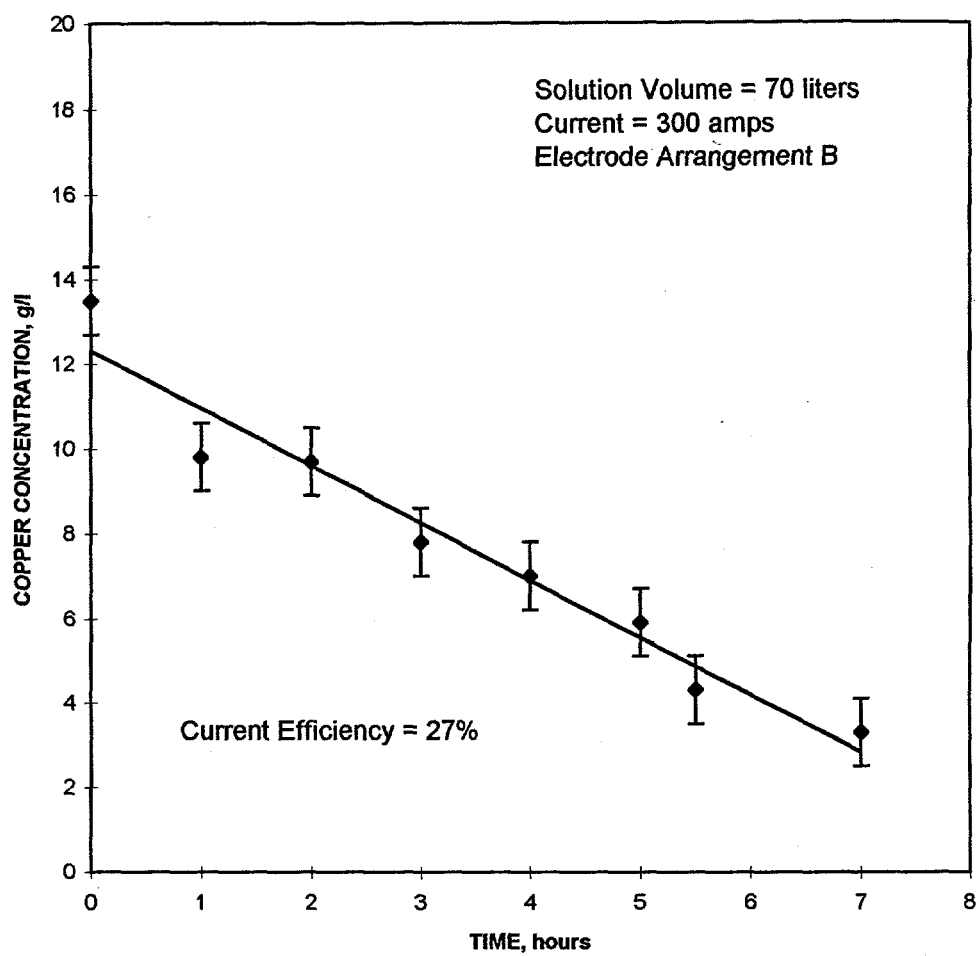
Figure 4. Change in copper concentration with time for a typical Phase II experiment using Electrode Arrangement B.

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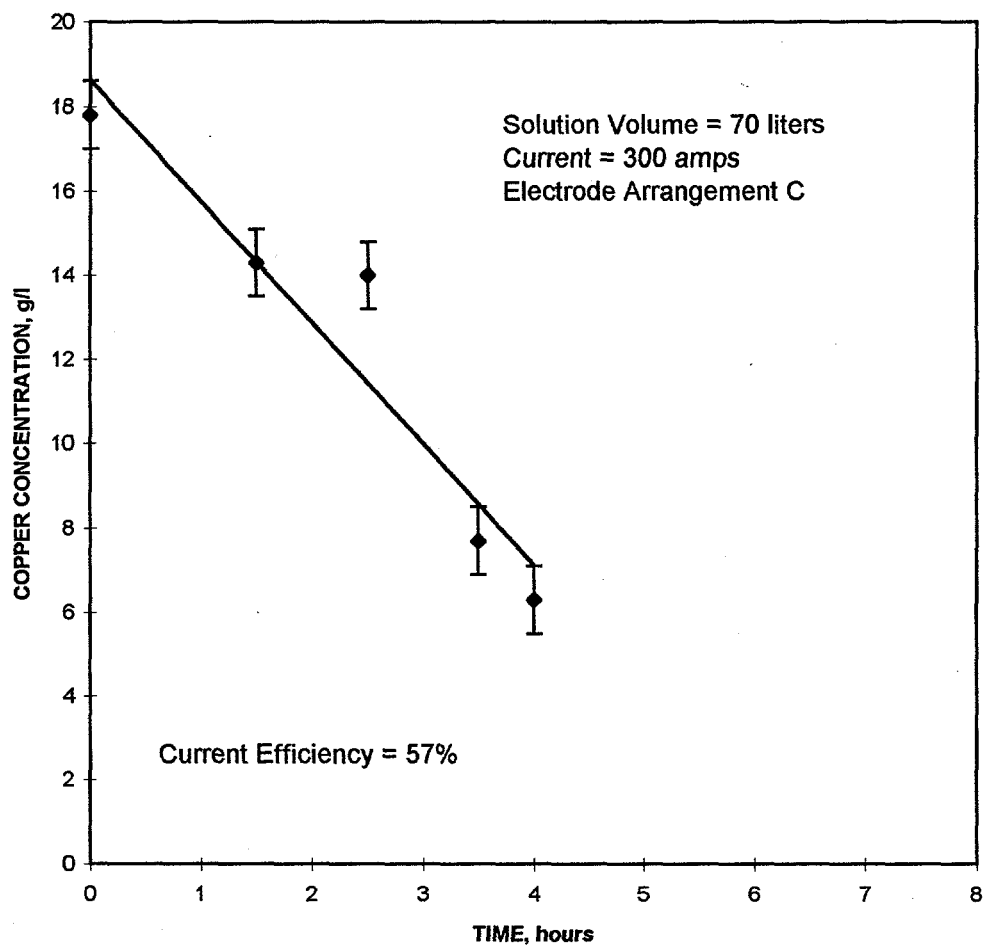
Figure 5. Change in copper concentration with time for a typical Phase II experiment using Electrode Arrangement C.

IV. OBJECTIVES AND APPROACH

The objectives of the Phase III study were to:

- Design and construct a 10,000-amp fluidized bed electrowinning cell for the recovery of copper from acidic sulfate solutions;

- Demonstrate the technical feasibility of continuous particle recirculation from the electrowinning cell with the ultimate goal of continuous particle removal; and

- Measure cell efficiency as a function of operating conditions.

The project was divided into seven identifiable tasks. Each is described below as presented in the contractual document with the Department of Energy.

Task 1 - Design Cell: Design a 10-kA fluidized bed copper electrowinning cell, advancing previous designs at smaller scale, with the objective of achieving reliable and efficient operation. The design will consider such factors as fluid flow and velocity, fluidization, stagnation, metal deposition, product removal, number and placement of electrodes, current efficiency, electrolyte separation materials, and oxygen removal.

Task 2 - Perform Design Review: Form a "Hazards and Operability" (Haz-Op) team and perform a Haz-Op review to assess the design and selected components, and to identify potential malfunctions and safety hazards. Modify the design (if required) as recommended by the Haz-Op team.

Task 3 - Construct Cell: Procure custom fabricated components, construct the electrowinning cell, and install the cell and the auxiliary equipment in the experimental operating area. Verify the instrumentation readiness.

Task 4 - Perform Materials Handling Tests: Shakedown the equipment by performing material handling tests in a safe manner using water. The objectives are to ensure that: (a) all equipment is properly installed and leak-proof, (b) operators are trained in emergency scenarios, (c) operational procedures are satisfactory for starting and stopping fluidization without excessive particle "leakage" through the distributor plate, (d) oversized particles are collected by the screen without plugging with near-sized particles, (e) the bed can be filled and emptied, and (f) the electrodes can be withdrawn for inspection and replacement.

Task 5 - Perform Handling Test Review: Conduct a Haz-Op team review of the equipment performance during material handling tests. Institute equipment modifications, if any, as recommended by the Haz-Op team.

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Task 6 - Provide an Experimental Plan: Develop an experimental plan, identifying operating variables to be investigated and the criteria for evaluating successful operation. Submit the plan to DOE for approval.

Task 7 - Perform Electrochemical Tests: Perform electrochemical tests to develop commercial conditions and to prove commercial viability. Perform large-scale experiments (nominally five) targeted for 8 hours of operation in keeping with the experimental plan. The specific objectives of these experiments are to define the: (a) cell current-voltage relationships, (b) correlations between productivity, current density, and fluidization (c) current efficiency as a function of copper concentration, and (d) energy required per unit of produced copper as verified by material balances. However, in the event that the experiments are prematurely terminated (because of poor current efficiency, evolution of copper at cathodes, electrical short circuits between electrodes, equipment failure, or other problems), evaluation of and changes to operating procedures will be accomplished before conducting additional experiments. Should the suspected controlling parameters (current density and fluidization) not be found to be paramount, decreased bed height, increased electrode spacing, or other changes may have to be instituted.

Task 8 - Report Project Results: Report acquired data and project results. Reports will include monthly verbal status reports including incurred costs, quarterly written reports, a final report for public dissemination, and a final review meeting with DOE and its technical representatives.

V. SYSTEM DESIGN

A. Fluidized Bed Cell

The cell body for this study was constructed of polypropylene (1.3 cm thick) covered with fiberglass-reinforced plastic. It was built in flanged sections for ease of installation and dismantling. A drawing of the body giving dimensions and delineating the various functional regions is given in Figure 6.

Solution entered the bottom-most compartment of the cell, denoted the feed plenum. The injection pipe entered through the side of the plenum and discharged downwards after passing a 90-degree elbow. Immediately after discharging through the elbow, solution encountered an impingement plate that directed flow to the periphery of the cell. Situated on the deflection plate was a polypropylene ball, 10 cm in diameter. When solution flowed through the feed pipe, the ball served to distribute solution onto the impingement plate. If flow was interrupted, the ball floated upwards and sealed the feed pipe to prevent rapid backflow of solution (and more importantly, particles) down the line into the surge tank. As much space as possible (about 15 cm) was left between the deflection plate and the distributor plate to allow fluid streamlines to straighten before liquid entered the distributor plate. The feed plenum had a conical bottom with a discharge valve to allow periodic removal of any particles that may have accumulated.

The distributor plate was constructed of 3.8-cm thick polypropylene. Approximately 6000 specially designed holes were individually drilled into the plate. Figure 7 shows a cross-section of one of the holes giving dimensions. The holes, 2 mm in diameter, were drilled through the plate in a hexagonal pattern with a spacing of 0.96 cm. (Hole diameter was selected to give a pressure drop through the distributor plate of 10% of the total pressure drop through the cell. Calculations were performed using well-known hydraulic correlations and will be discussed in greater detail in Chapter VI.) The holes were countersunk from the top at a 20° angle. This removed all horizontal surface from the top of the distributor plate, giving it a honeycomb appearance. Any particle large enough to fall to the bottom of the fluidized bed and encounter the distributor plate would be forced towards the center of a hole where the upward velocity would be sufficiently high to throw the particle upwards, back into the bed.

Immediately above the distributor plate was the working volume of the cell. This section was 79 cm in height. Two discharge ports were installed near the bottom of the working volume as close as possible to the distributor plate. One, 5 cm in diameter, was for continuous removal of particles to be recycled to the top of the cell and the other port, 7.6 cm in diameter, was for emergency discharges. Ideally, the discharge ports would have been situated on the distributor plate. However, construction details did not allow this and the lower-most point in the discharges was located about 1 cm above the top of the plate.

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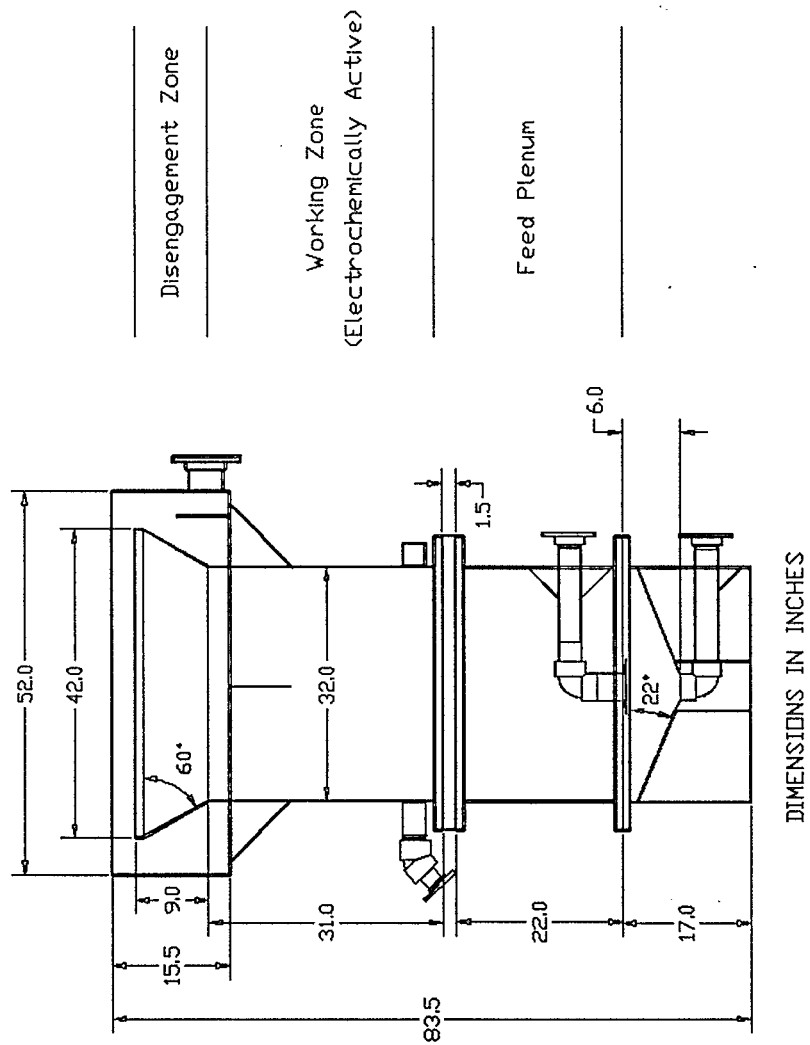
Figure 6. Dimensional drawing for Phase III fluidized bed cell showing functional areas within the unit.

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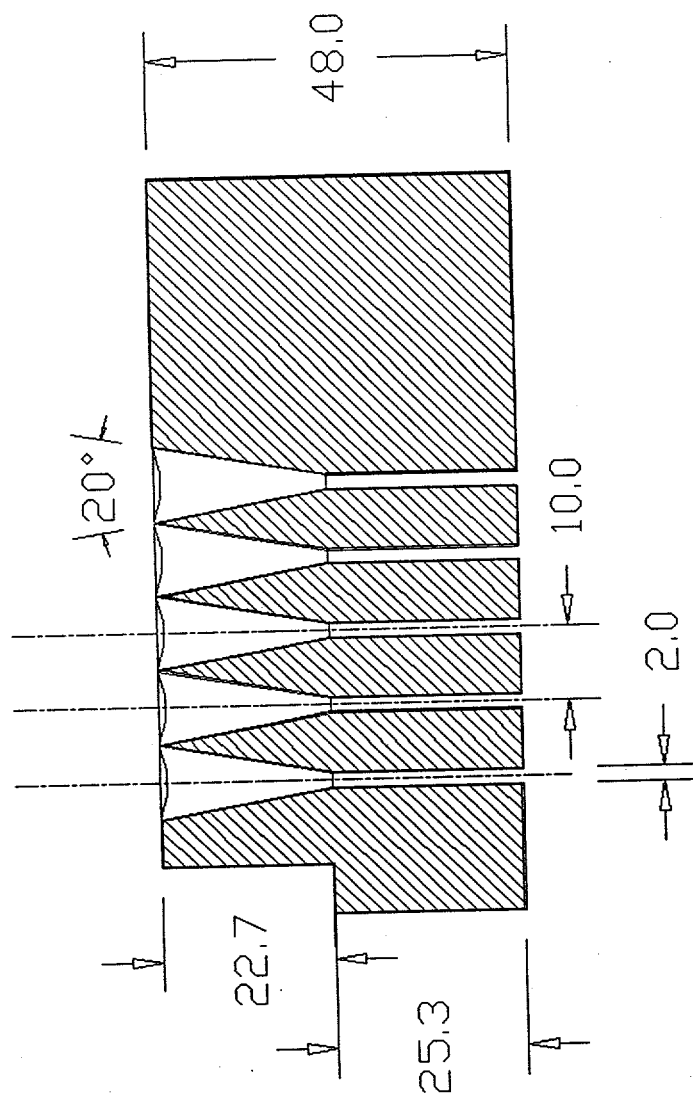
DIMENSIONS IN MILLIMETERS

Figure 7. Distributor plate details for Phase III fluidized bed cell.

The disengagement zone was immediately above the working volume. Here the internal diameter of the bed flared from 81 cm to 107 cm, slowing the superficial velocity and allowing fine particles entrained in the flow to settle back into the bed. Solution overflowed the top of the cell around its entire periphery and was captured in a collection chamber. From there it overflowed an adjustable weir back to the surge tank. A screen was installed above the weir to trap any particles that might have been carried out of the cell (for example, by attachment to bubbles).

B. Electrode Construction and Arrangement

Anodes for the fluidized bed electrode were the single largest cost item in the construction of the fluidized bed electrowinning system. After discussions with a number of electrode manufacturers, including one producing ceramic electrodes, coated titanium mesh anodes manufactured by Eltech Systems Corporation were selected. A construction drawing for the anodes is given in Figure 8. As indicated, the anodes were cylindrical with a diameter of 7.6 cm and a length of 122 cm. The anodes were constructed of expanded titanium mesh coated with a proprietary catalyst to promote oxygen generation. Running down the center was a titanium-clad copper rod to distribute current over the anode surface and through which the anode was connected to the busbars.

A 0.3-mm thick porous polypropylene membrane was used to separated cathodic particles from anodes. The material was manufactured by the W.R. Grace Company under the trade name of Daramic and is commonly used as a separator in automotive batteries. Installing the membrane around the anodes proved a difficult task. Initially, the membrane was simply wrapped around the anodes and sealed along one edge with silicone sealant. Later a double wrap of Daramic was used. Strips of duct tape provided extra support at the top and bottom of the anodes along with one strip in the middle.

At the start of the program, the membrane was applied directly over the anode. After discovering copper dendrites had bridged through the membrane, a layer of polypropylene screen (35 mesh) was applied between the membrane and the anode. This provided a gap of 0.5 mm between the anode and the membrane. Later, this was doubled by wrapping the polypropylene mesh around the anodes twice. In the final configuration, strips of 4 mesh screen with a thickness of 2.5 mm were placed on the anodes before wrapping with the 35 mesh screen giving a gap of 3.5 mm. After applying the screen and membrane, a polypropylene cone was attached to the bottom of each anode to provide a hydrodyamically smooth surface to promote fluidization. The cone had an angle of about 70 degrees.

For cathode current feeders, copper bar stock of 15.9-mm diameter was used. The current feeders were arranged around the anodes as shown in Figure 9. The design was similar to the final electrode arrangement studied in Phase II. The spacing between anodes and current feeders was about 2.5 cm.

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Figure 8. Construction details for Phase III anodes.
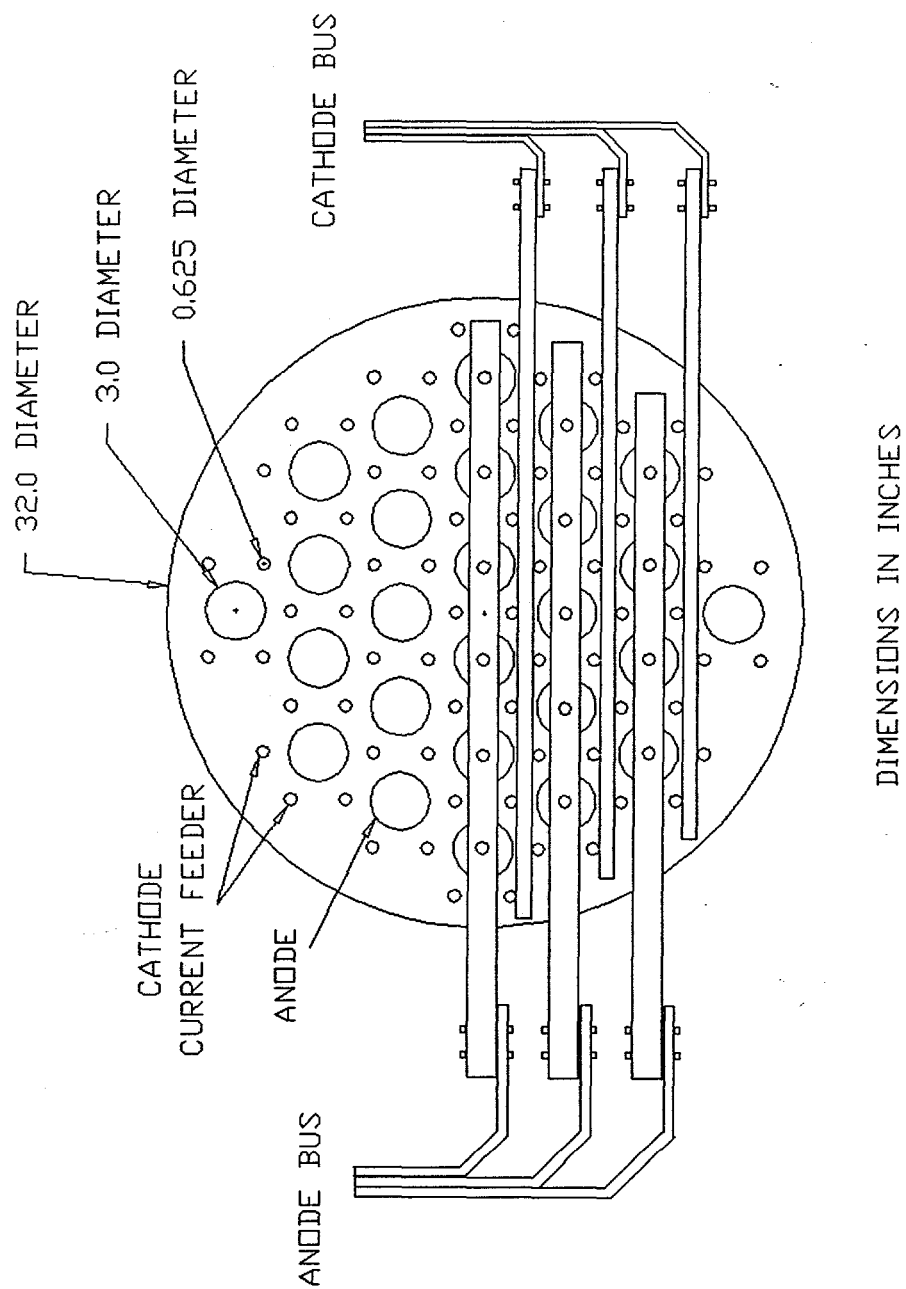
Figure 9. Geometrical relationship between anodes and cathode current feeders in Phase III fluidized bed cell.

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C. Auxiliary Equipment
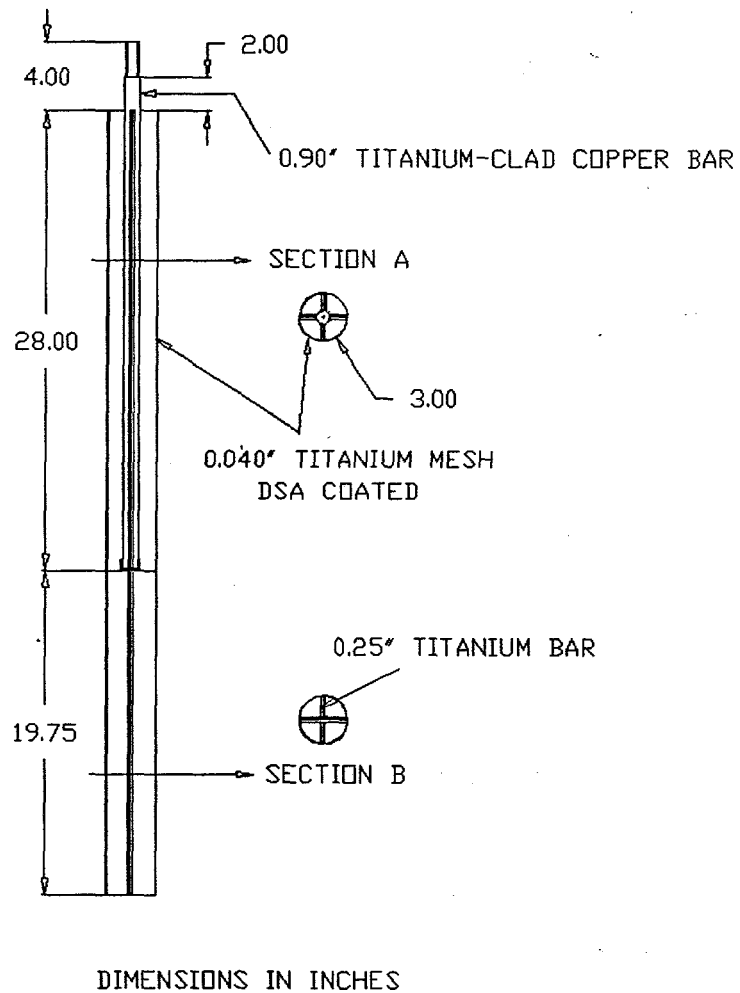
Auxiliary equipment for the fluidized bed system included the fluid handling system to provide solutions for electrowinning, a DC electrical source and appropriate instrumentation.

The "Piping and Instrumentation" diagram for the fluidized bed system is shown in Figure 10. As indicated, the fluidized bed reactor was connected to two tanks through a series of pipes. (All piping for the installation was constructed of butt-weld polypropylene.) Tank T-751, the system surge tank, provided solution for the fluidization pump P-752, the recycle pump P-751 and the anode solution pump P-753. All solutions in the system, originating from the same tank, had the same composition. Fluidization solution (catholyte) entered the bottom of the fluidized bed reactor and flowed upwards, causing particles inside the bed to fluidize. As the solution flowed upwards in the working zone of the cell, copper deposited from solution onto the particles. The concentration of copper in solution was therefore slightly lower leaving the bed than it was upon entering. Catholyte overflowed the top of the fluidized bed reactor and returned by gravity to the surge tank T-751.

Recycle solution was used as a carrier for copper particles that flowed out of the bed through an eductor. Solution from surge tank T-751 was pumped through the eductor as the motive fluid, creating a negative pressure and drawing particles out of the fluidized bed. Particles were transported upwards to a selector valve. Depending on the position of this valve, particles were either returned to the top of the fluidized bed reactor or were pumped into storage tank T-752. The recycle stream was therefore the source of a particle "harvest". Particles could be recovered from the system whenever the selector valve was positioned to do so. This was done periodically depending on operating conditions. Particles were retained in the storage tank but solution overflowed into the surge tank T-751. Similarly, particles returning to the bed flowed downwards into the fluidized cathode with solution commingling with catholyte.

An eductor was necessary for the Phase III installation but not for the Phase II work because of the increase in height differential between the bottom of the fluidized bed and the top of the storage particle storage tank. (In the Phase III installation, this elevation was over 4.6 m.) The combination of this pumping height and frictional losses in the line meant that a substantial pressure had to be overcome to allow particles to flow out of the base of the fluidized bed. A commercially available eductor was purchased and installed. The unit had 3.8-cm connections on the suction and discharge sides and a 1.3-cm motive connection.

Anode solution (anolyte) was pumped from tank T-751 by pump P-753. It flowed to the top of the fluidized bed reactor into a distribution manifold that divided the flow into 26 equal streams feeding each of the 26 anodes. Solution traveled in a flow tube to the bottom of the anode and then flowed upwards, overflowing into catholyte which in turn overflowed into the surge tank. Anolyte and catholyte therefore commingled at the top of the bed before being returned to the surge tank. (Mixing of oxygenated anolyte with catholyte provided the oxidant for copper

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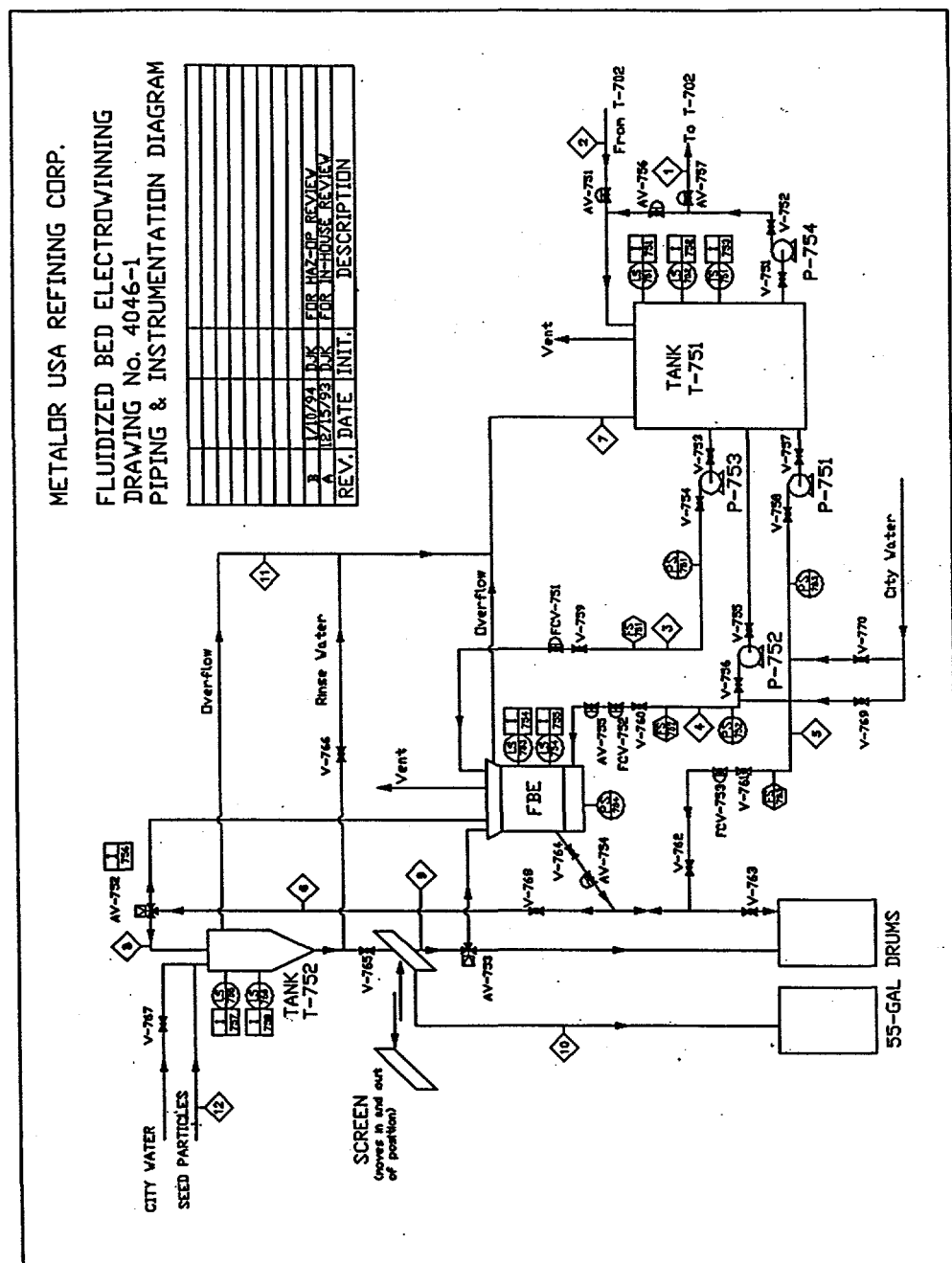
Figure 10. Piping and instrumentation diagram for Phase III fluidized bed system.

dissolution into sulfuric acid electrolyte and reduced current efficiency, discussed below.) A manifold could have been provided to keep anolyte separate from catholyte. This would require a separate anolyte holding tank but have two advantages: (a) oxidation products from the anode would be kept away from particles in the fluidized cathode; and (b) anode reactions other than the oxidation of water could be investigated.

The copper concentration in the surge tank would continuously fall (assuming no dissolution of copper within the bed) without an external source of copper sulfate solution. The external source in this investigation was an operating sulfate leaching system connected to the surge tank T-751 through pump P-754 and its associated piping. Solution from the leaching circuit continuously flowed into tank T-751, raising its level. At a predetermined point, measured by the level sensor in the tank, a programmable logic controller activated the automatic valves to return solution to the leaching circuit. The level in the surge tank then fell to a predetermined point at which flow to the leaching circuit would stop. The level in the surge tank was therefore maintained between two control points. The concentration in the tank was determined by the relative rates of copper deposition on the cathode and solution addition from the leaching circuit. The flowrate of leach solution could be varied to maintain a constant copper concentration in the tank as measured by samples taken by operators on a periodic basis. If the concentration fell with time, the flow rate of leach solution was increased. Conversely, of the copper concentration increased with time, the flow rate of leach solution was decreased.

The rectifier for the system was a thyristor unit providing constant current or constant voltage depending on its operating mode. In these experiments, voltage was allowed to fluctuate at a specified current. The maximum output of the unit was 10,000 amps at 18 volts DC.

Instrumentation consisted of pressure gages and manometers for pressure readings, a pressure transducer for surge tank volume and an impact-type flow meter for fluidization flow. Recycle flows and anolyte flows were measured with paddle-type flow meters. The most challenging measurement concerned the degree of bed expansion. Here an optical sludge gauge was successfully employed. This unit consisted of an 84-cm long probe with a "U" cross-section. LED light sources were mounted on one side of the "U" opposed by light sensors on the other side. Pairs of sources and sensors were mounted every 0.5 cm along the probe's length. The green-blue light produced by the diodes was visible to detectors through saturated copper sulfate solutions. As the bed expanded, light from the sources would be obscured, allowing bed height to be determined.

Figure 11 gives a three-dimensional view of the entire installation showing the physical relationship between the various pieces of equipment. The system was constructed on two levels with the surge tank and pumps located on the lower level and the rectifier and control panel on the second level. The fluidized bed was positioned between the two levels to allow access to the electrodes. The particle storage tank was suspended above the fluidized bed.

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Storage Tank
T-752

Screen

Fluidised Bed Reactor

Rectifier

Surge Tank
T-751
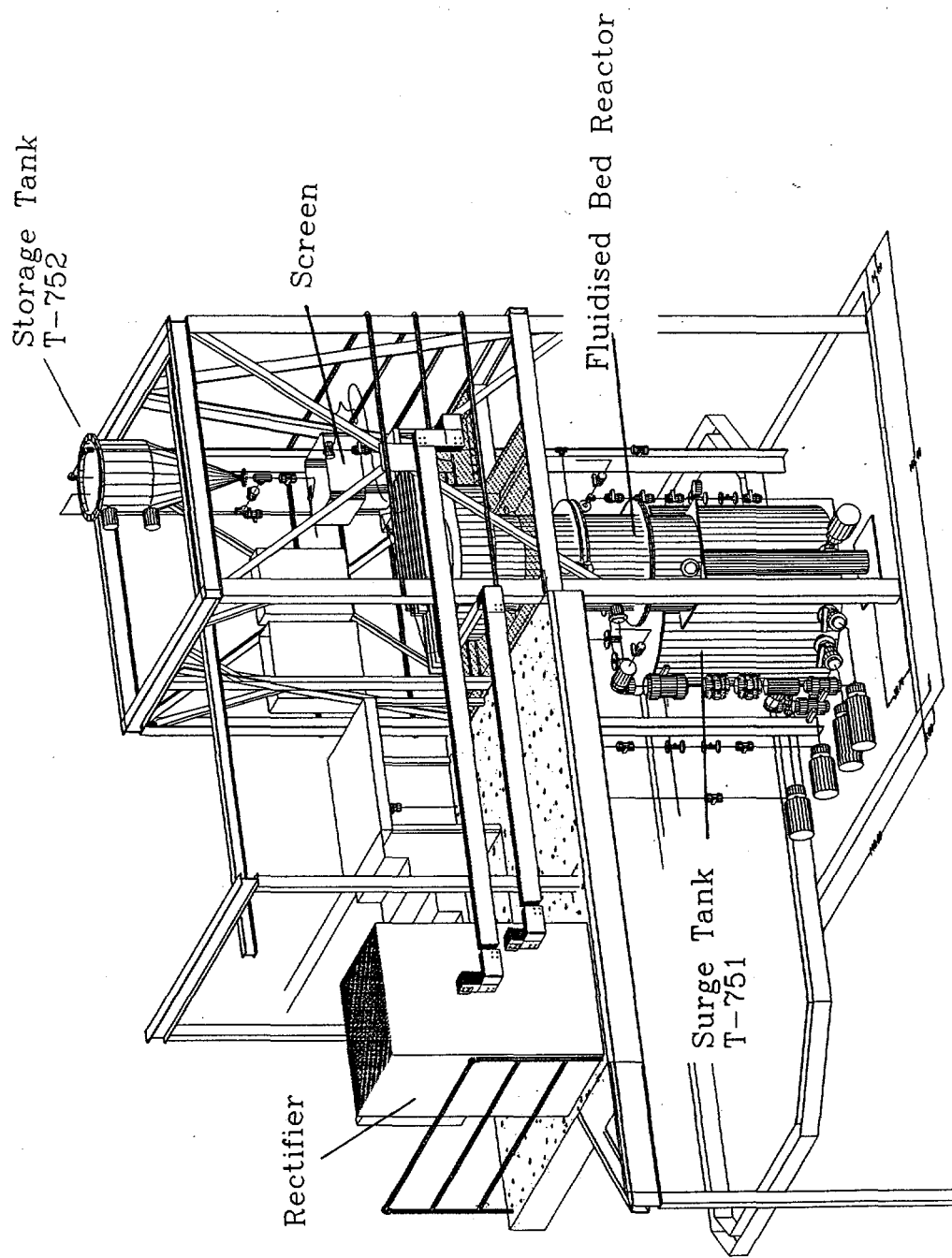
Figure 11. Spatial relationship of equipment in Phase III fluidized bed system.

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D. Particle Size Considerations

The most problematic aspect of Phase II experiments was the formation of particle clusters within the fluidized cathode. These clusters, developing from the surface of a current feeder, grew over time until a short circuit developed between electrodes causing experiments to be halted. The cause of the accretions was believed to be areas of poor fluidization with high or low bed densities. Because these areas were not distinguished by a particular position in the bed (although areas where electrodes were not properly aligned resulting small gaps between electrodes were prone to these accretions), it was concluded that overall fluidization was to blame. Measures were therefore taken to improve the fluidization in the Phase III design. These included replacing the conical distributor plate from Phase II with a flat plate in Phase III and reducing wall effects by increasing the diameter-to-height ratio from 0.16 in Phase II to about 1 in Phase III. Lastly, the size of the particles was reduced in order to maintain smooth or particulate fluidization within the cathode.

Smooth fluidization contrasts with bubbling or aggregative fluidization found in most gas-solid fluidized beds. In aggregative fluidization, bubbles of fluid devoid of particles work their way upwards through the bed. Because of these fluid bubbles, areas of high and low bed density exist. Areas of high bed density near a current feeder could lead to particle clusters becoming attached to the current feeder impairing fluidization in the immediate vicinity and ultimately resulting in a short circuit. Areas of low fluidization prevent charge from being transported into the bed and result in dendritic growths on current feeders. Unless the fluctuations in density change rapidly, both upwards and downwards shifts are undesirable.

Several investigators have studied the transition from smooth to aggregative fluidization and it was apparent from this body of work is that the key variable determining whether a system displays smooth or aggregative fluidization is particle size. Fine particles fluidize smoothly while coarse particles result in bubbles. The point at which the transition occurs is not clearly defined and one must rely on generalized correlations for guidance.

Davidson and Harrison[21] developed a bubble stability condition with which the maximum bubble size in a given fluidized bed can be estimated. By supposing that in smoothly fluidized beds the size of the bubbles is roughly equal to the size the particles whereas in an aggregative bed, the bubbles are ten times larger, a model was constructed to predict the behavior of a given system. Using this approach, the transition region for spherical copper particles fluidized by water is between 100 and 200 microns. Wilhelm and Kwauk[22] found that the dimensionless Froude number distinguished between the two modes of operation, and suggested:

$$Fr_{mf} < 0.13 \qquad \text{smooth fluidization}$$

$$Fr_{mf} > 1.3 \qquad \text{aggregative fluidization}$$

where the subscripts refer to conditions at minimum fluidization and the Froude number is defined as:

$$Fr_{mf} = u_{mf}^2 / d_p g$$

with u_{mf} denoting flow velocity at the point of minimum fluidization and g the gravitational constant. For spherical copper particles in sulfate solutions, the transition between the two types of fluidization begins at 1.2 mm (using the general equation for minimum fluidization velocity given by Kunii and Levenspiel[23]). Romero and Johanson[24] went further. After considering stability equations for the bed-fluid interface (originally proposed by Rice and Wilhelm[25]), these investigators suggested four parameters to characterize fluidization behavior:

$$F_{mf} \qquad Re_{p, mf} \qquad (\rho_s - \rho_l) / \rho_l \qquad L_{mf} / d_b$$

where $Re_{p, mf}$ is the particle Reynold's number at minimum fluidization, ρ_s and ρ_l the particle and fluid densities, respectively and L_{mf} and d_b the bed height and diameter at the point of minimum fluidization. An increase in any of these parameters causes instability in the bed leading to bubble formation. (The importance of wall effects is given explicitly in the fourth parameter.) Romero and Johnson proposed that if the product of these four parameters was less than 100, the bed would be stable and smoothly fluidize. In the case here, this corresponds to a maximum particle size of 390 microns if the spacing between electrodes (2 cm) is used to represent bed thickness.

Based on these calculations, one can conclude that aggregative fluidization was indeed occurring in the Phase II apparatus where the maximum particle size approached 2000 microns. Whether aggregative behavior is a sufficient condition for the formation of accretions in fluidized bed electrodes is open to debate and will be discussed further in the experimental section. But it was felt that aggregative flow contributed to the development of accretions in the Phase II work and to prevent such flow in Phase III, a substantially finer particle size distribution was selected from commercially available copper shot. The size distribution is given in Table 3 and shown graphically in Figure 12a. The mean size for this material was about 0.2 mm (200 microns). With a maximum particle size of about 250 microns, the Phase III size distribution easily met the Wilhem and Kwauk and Romero and Johnson criteria for smooth fluidization. The criterion of Davidson was not met (250 microns versus a limit of 100 to 200 microns), but was within a factor of two of this roughly defined limit.

After performing a number of experiments with these fine copper particles in which difficulties were experienced (described in later sections), we opted for a much coarser distribution. Instead of copper, conductive graphite particles were chosen to make it easy to distinguish areas in the bed where copper deposition occurred. The "as-received" graphite was wet screened at 16 mesh to remove fines before being charged to the bed. The size distribution of the graphite particles is given in Table 4 and shown in Figure 12b. The mean size for these particles was about 2 mm, ten times larger than the copper particles.

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Table 3. Size Distribution of Copper Particles for Phase III Fluidized Bed Experiments.

Size Mesh	Size microns	Weight Percent in Interval
+60	+250	1.6
60 to 70	210 to 250	53.2
70 to 80	180 to 210	34.5
80 to 100	150 to 180	9.4
100 to 140	106 to 150	1.4

Table 4. Size Distribution of Graphite Particles for Phase III Fluidized Bed Experiments.

Size Mesh	Size millimeters	Weight Percent in Interval
+6	+3.35	0.06
6 to 8	3.35 to 2.36	31.52
8 to 14	2.36 to 1.41	58.63
14 to 16	1.41 to 1.18	9.80
-16	less than 1.18	0.00
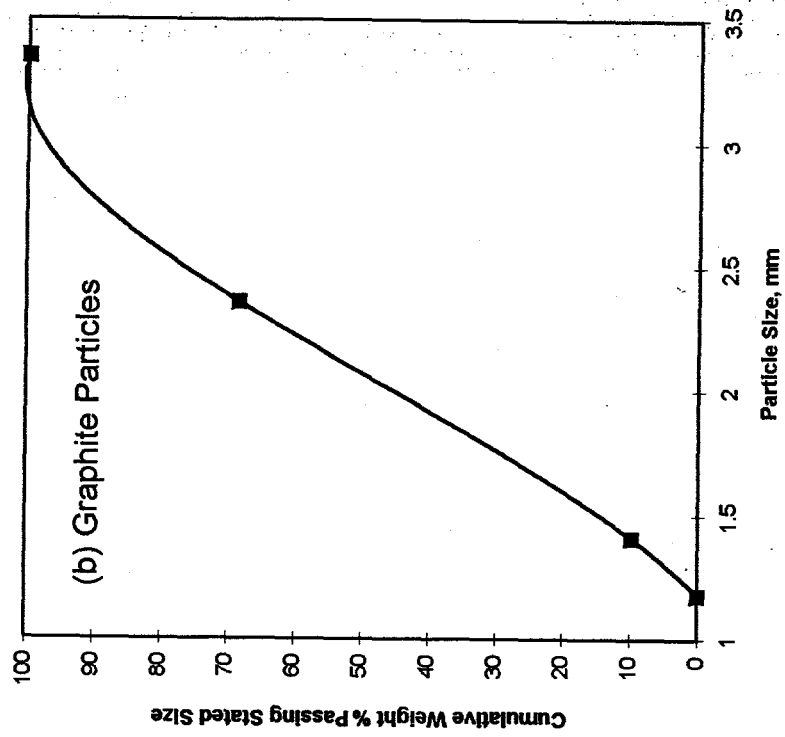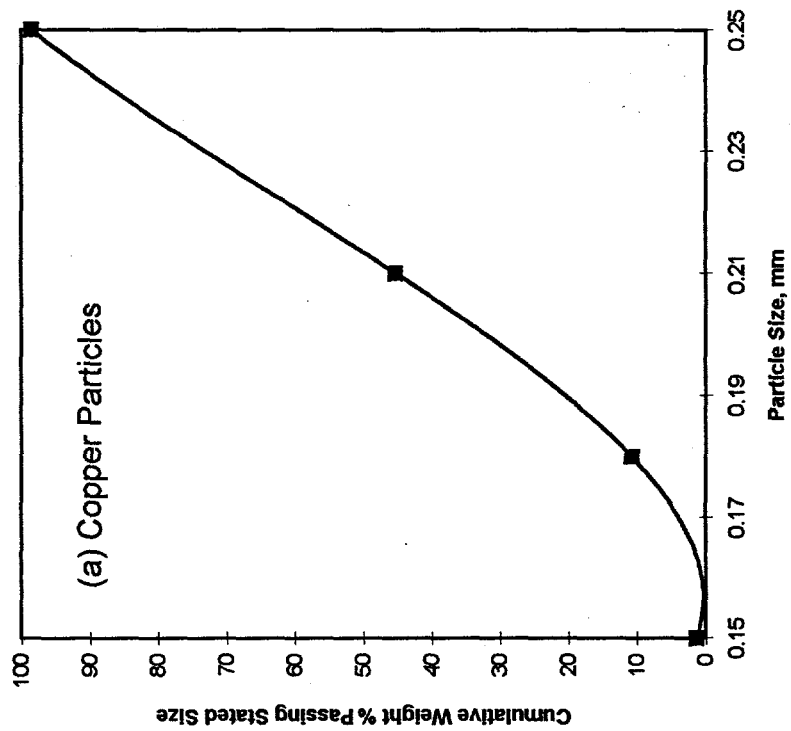
Figure 12. Size distribution of particles used in Phase III fluidized bed experiments: (a) copper particles and (b) graphite particles.

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E. Changes from Phase II Design

The 10-kA Phase III cell incorporated several design changes from the 1-kA Phase II cell. The most significant change was its larger diameter. But other significant changes were made to achieve uniform fluidization within the bed. The conical distributor plate was replaced with a flat design and particle discharge occurred at the periphery of the bed rather than at the center. The feed plenum was substantially expanded to give more space for parallel streamlines to develop before the fluid entered the distributor plate. The direction of the flow into the plenum was aimed downwards against a circular deflection plate to distribute the flow around the plenum. The aim of both these measures was to promote uniform pressures at the base of the distributor plate.

The other significant changes evolved from particle considerations. Since large particles could fall to the bottom of the fluidized bed and settle on the distributor plate, the hole design was changed from a slightly tapered cross-section to a conical cross-section. The aim here was to eliminate any horizontal surface on which a particle could lodge. Large particles, falling to the bottom of the bed, would be forced into a region of high velocity and be entrained back in to the bed. Eventually, these particles would report to the side discharge by random walk. Lastly, the size distribution of particles constituting the fluidized cathode was shifted to the finer sizes to promote smooth fluidization rather than aggregative fluidization in the hope of eliminating areas of fluctuating bed density and the resulting formation of particle accretions.

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VI. MATERIALS HANDLING EXPERIMENTS

The objectives of the materials handling experiments were to ensure that: (a) all equipment was properly installed and leak-proof using water as a safe testing fluid; (b) procedures and equipment were adequate for starting and stopping the bed and that operators were properly trained; and (c) fluidization parameters of the bed were delineated in preparation for electrochemical experiments. A summary of the various experiments performed as part of our evaluation of the materials handling aspects of this project is presented in Table 5.

A. Safe Fluid Testing

Before accepting the fluidized bed cell from the manufacturer, the constituent parts were assembled in the factory and a static water test was performed for a period of 48 hours. No leaks were found around any of the flanged connections. The cell was then dismantled and shipped to Metalor USA Refining Corporation.

Once the equipment was installed and piping completed, water was used to check the integrity of all welds and flanged connections. Several leaks were found and corrective measures taken. Once all leaks were corrected, the piping contractor was released and the installation deemed complete. Operating procedures (presented in Appendix B) were reviewed in a Hazards and Operability review and found to be adequate.

Instruments were checked and calibrated where necessary. The two most crucial instruments were the depth gage used to determine bed height and the flow meter on the fluidization line. Both were found to be reliable and accurate. The impact-type flowmeter used to measure fluidization flow was checked by measuring the time it took to fill the upper portion of the cylindrical fluid bed reactor. The calibration curve for the flow meter in presented in Figure 13. The depth gage was checked by comparing it reading against bed height measured from the top of the reactor down to particle height. The only time the depth gage readings were found to be inaccurate was when the solution became too turbid to be penetrated by the light sensors. This occurred rarely when either the acid concentration was too low resulting in hydroxide formation or when fresh graphite particles were just added to the bed.

Also measured was the overall solution volume of the system. This volume consisted of solution in the holding tanks and the fluidized bed along with the piping making up the pumping system. In addition to estimating system holdup based on simple geometrical calculations, overall volume was checked by adding a known weight of sodium sulfate to the system and measuring the sodium concentration in solution after equilibrium had been reached. Sodium was analyzed by direct current plasma spectroscopy. System volume was calculated by dividing the known weight of sodium added by the measured concentration. Incremental additions of sodium sulfate were made four times and after each addition, the sodium concentration was measured at least three and

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Table 5. Summary of Phase III Materials Handling Experiments.

| Experiment	Focus	Findings
M1	Impact flow meter	Measured flow is slightly greater than flow from impact meter; calibration factor determined
M2	Heating due to pumps	Temperature of solution increased from 40C to 52C in 16 hours; stabilized at 52° C
M3	Fluidization	First addition of copper particles to system
M4	NaCl tracer test	Determined volume of system using known sodium addition then measuring concentration
M5	Packing density particles	Measured packing density of copper particles at 5.375 gm/cc
M6	Copper circulation	Began circulating copper from bottom of bed to top; solids circulation rate of 600 cc/min
M7	Fluidization	Lost power during run; copper particles drained through distributor plate to storage tank
M8	Fluidization	Measured flow vs fluidization curve
M9	Distributor pressure drop	Installed manometer to measure pressure drop across distributor plate
M10	Fluidization	Recorded fluidization vs flowrate on video; non-uniform fluidization below about 20% expansion
M11	Fluidization	Power failure interrupted run; decided to install distributor plate with smaller holes
M12	Particle circulation	By increasing pumping rate past eductor, recirculated copper particles to upper storage tank
M13	Recirculation flow meter	Calibrated recirculation flow meter in gpm
M14	Distributor pressure drop	Measured pressure drop across new distributor plate; significantly higher than old plate
M15	Sulfate electrolyte	Sulfuric acid electrolyte; in 72 hours, copper in solution increased from 9.6 to 14.3 g/l
M16	Distributor plate	Pressure drop across distributor plate climbed during run; acid decreased as copper increased
M17	Size distribution	Sampled bed and checked size distribution of particles to see if dissolution affected size
M18	Storage tank	Emptied storage tank and found copper particles near inlet to fluidization pump
M19	Distributor plate	Removed distributor plate and found holes plugged with solution debris; particles between plates
M20	Distributor plate	Operated for 3 days without pressure buildup using 2 mm holes; copper dissolution continuing.
M21	Oxygen uptake.	Installed air tube and flow manifold to control uptake of oxygen by leach solution
M22	Solution ORP	Installed ORP probe to measure if efforts at controlling oxygen uptake were successful
M23	Particle size	Added larger copper particles to bed to increase overall size distribution
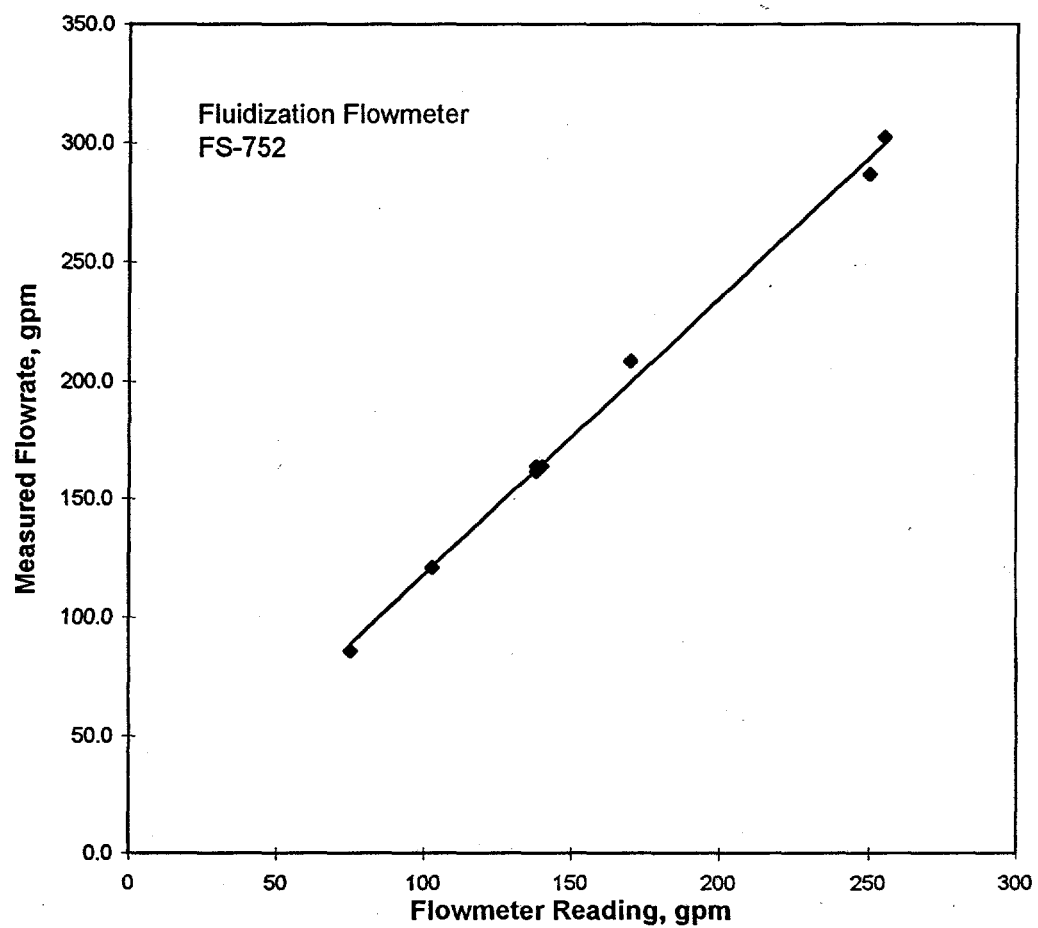
Figure 13. Calibration curve for fluidization flowmeter.

usually four times. The average concentration at each level was then calculated as was the change in concentration with each addition. These four concentration changes were then averaged to calculate system volume. This value (2325 l) was within 5% of the volume calculated from tank sizes (2432 l). The small difference between the two volume methods of volume measurement has no significant bearing on calculations of current efficiency presented in later parts of this report.

B. Pressure Drop through the Distributor Plate

As part of initial experiments, measurements were taken of the pressure drop through the distributor plate as a function of flowrate. Pressure drop readings were taken with a manometer connected at the discharge port of the feed plenum; the fluidization flowmeter was used for flowrates. A plot of the pressure drop and the square root of the pressure drop versus flowrate is given in Figure 14. As shown, the data follow the usual square root dependence of the form:

$$u_{or} = C_d \left(2 \, g_c \, \Delta P_d \right)^{1/2} \rho_l^{-1/2}$$

where u_{or} is the orifice velocity, C_d the orifice coefficient, ΔP_d the pressure drop across the distributor plate, ρ_l the liquid density and g_c the mass/force conversion factor. The orifice velocity is computed by dividing the volumetric flowrate by the area of the orifices, which equaled 205.6 cm^2. Using the regression coefficients, including a non-zero intercept, the actual discharge coefficient was calculated to be 0.71 for this installation. This value is close to the value of 0.6 given in the literature for distributors at high Reynolds numbers. The fact that the actual orifice coefficient was higher probably relates to the thickness of the distributor plate used in these experiments.

Although the orifice coefficient turned out be greater than anticipated, the pressure drop across the distributor plate was less than expected. A review of the design specifications showed that the number of 2 mm holes drilled into the plate was greater than planned. This was due to: (a) a change in specifications for the hole pattern from a square design to an equi-spaced "close-packed" design; and (b) a slight variation in the actual spacing between holes. The net result was more holes and as a consequence the orifice velocity was lower than planned. However, since the feed plenum was specially designed to promote uniform flow (with the centrally located discharge aimed downwards to the deflection plate and a large distance between the deflection plate and the distributor plate), it is believed that the low pressure drops did not adversely affect fluidization within the bed at bed expansions greater than 20%. This could be clearly seen during initial experiments with water. By observing the top surface of the fluidized bed illuminated by a high-intensity light through the water, one could see that the bed was uniformly fluidized. At bed expansions less than 20%, the surface of the bed was not smooth, evidence that the flow in some orifices was higher than in others.
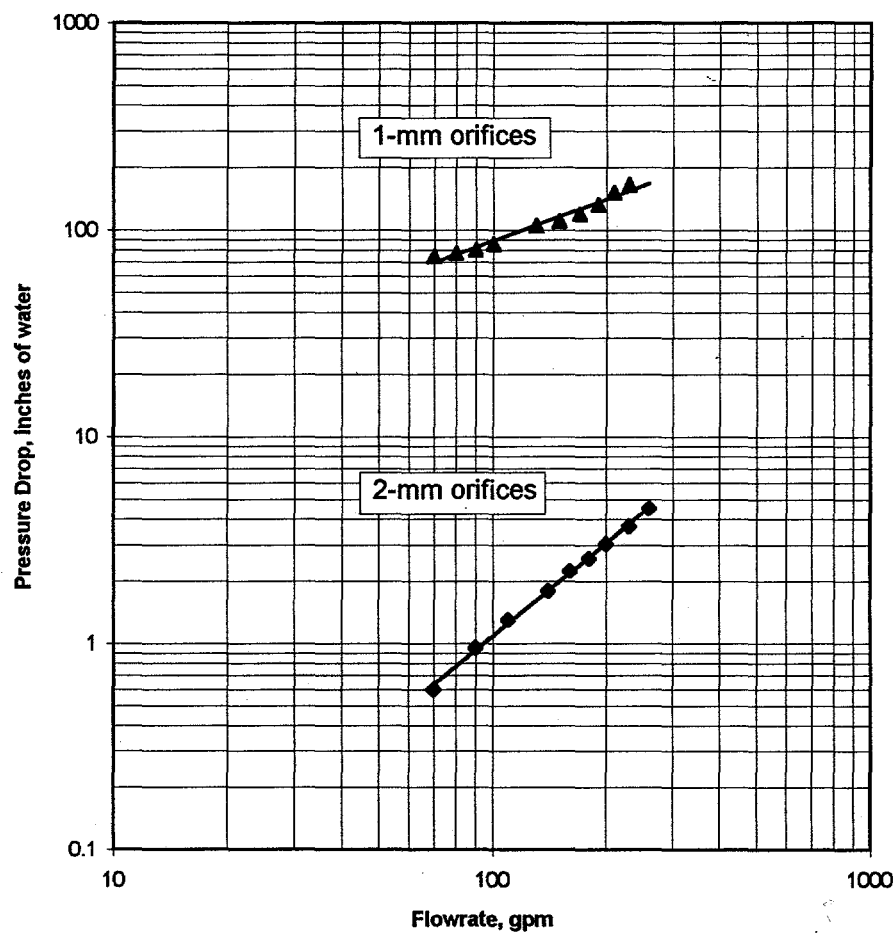
Figure 14. Pressure drop across the distributor plate as a function of flowrate for the two different hole sizes examined in this study.

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In order to attempt experiments at low bed expansions (less than 20%), it was decided to increase the pressure drop through the distributor plate by attaching a back plate with 1 mm holes. A 0.64-cm sheet of polypropylene was welded around its circumference to the distributor plate and attached in the center with several screws. Holes with a diameter of 1 mm were then drilled downwards from the top using the existing 2-mm holes as guides. As expected, the smaller diameter holes increased pressure drop through the distributor plate substantially. However keeping the holes unclogged during extended operation proved impossible. Particles, either weeping down through the deck plate or, having been carried over the top of the bed and subsequently pumped out of the storage tank, clogged the holes as experiments were in progress. (Particle "weeping", the transport of particles back through the distributor plate during fluidization, has been decried in the literature for gas fluidized beds.[26,27] While this mechanism was suggested to explain the plugging of the 1-mm distributor plate holes, a more likely cause was plastic debris from the drilling operation that had not completely been removed combined with fine particles of various materials normally found in industrial leach solutions.) By periodically stopping the flow and allowing some solution to drain back through the holes to free trapped particles, one could temporarily decrease pressure drops. But the particles that fell through the deck plate into the feed plenum when the flow was stopped would eventually become trapped in the holes again. After performing the initial electrochemical experiments with the 1-mm holes, it was decided to abandon the back plate and perform all experiments with the original 2-mm holes.

The degree of fluidization, expressed as percent bed expansion, as a function of flowrate through the distributor plate is presented in Figure 15. Data are given for two different sizes of copper particles, the "fine" particles being the copper particles described in Table 3 and used in Phase III fluidized bed experiments and the "coarse" particles being a mixture of particles from Phase II and Phase III experiments with an average size of about 0.5 mm. As expected, the bed did not begin to expand until a certain "minimum fluidization" velocity (corresponding closely to that calculated from the well-known equation given by Kunii and Levenspiel[23]) had been reached. Figure 16 gives the corresponding figure for the 2-mm graphite particles.

C. Particle Recycle Experiments

A primary objective of the materials handling experiments was to demonstrate that particles could be continuously recycled out of the bottom of the bed through a size separating device and back into the top of the fluidized bed. This would allow for continuous recovery of oversize particles constituting final product from the system. The need to periodically shut down the fluidized bed would therefore be eliminated.

A great deal of effort was devoted to the removal of particles from the bed. Design calculations showed that, unlike the Phase II installation, an eductor would be required to provide some suction on particles in the bed to overcome the head pressures needed to pump particles to the top of the storage tank mounted above the fluidized bed. Initial experiments showed this to be the case. In fact more suction was required than anticipated requiring that the head pressure be

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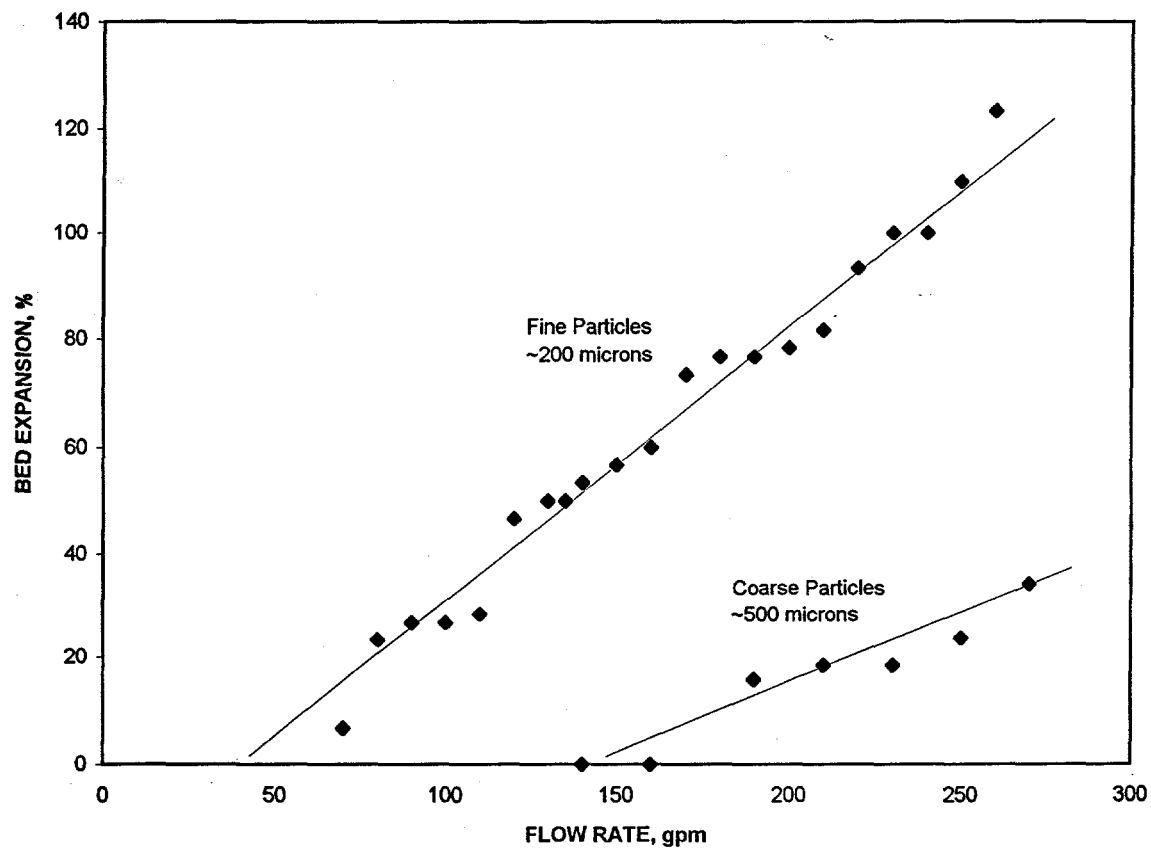
Figure 15. Bed expansion as a function of flowrate for copper particles.
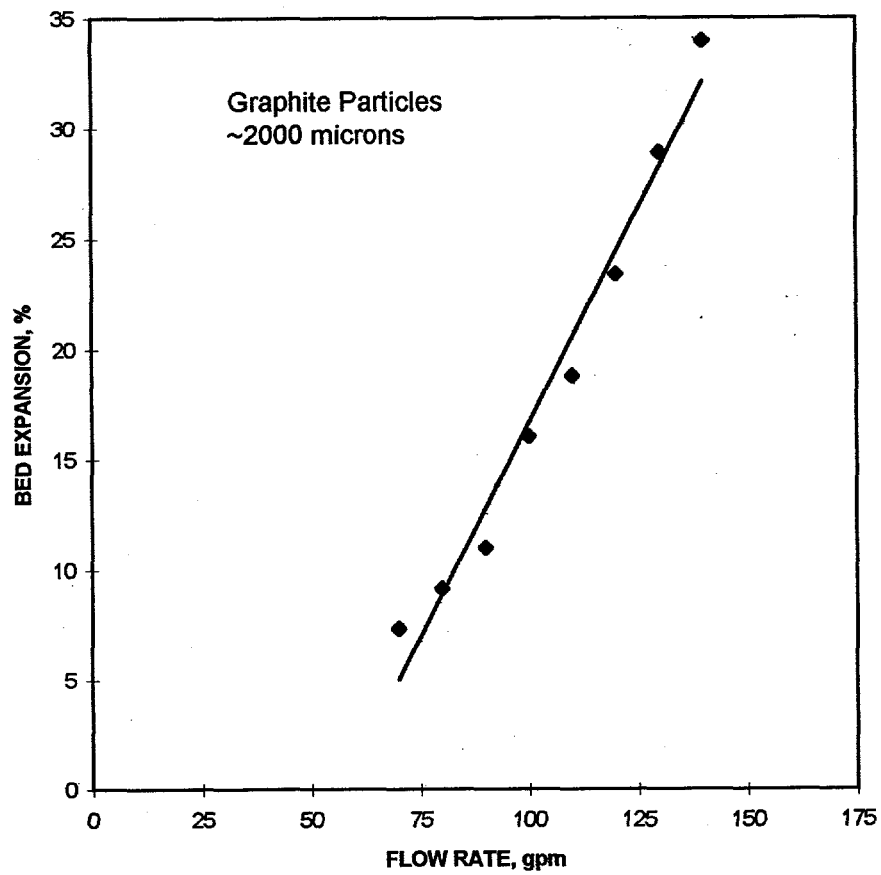
Figure 16. Bed expansion as a function of flowrate for graphite particles.

reduced by increasing the pipe diameter between the fluid bed discharge and the storage tank. Also the impeller of the recycle pump was increased to provide more flow. When these changes were accomplished, particle recycle could be performed without difficulty. It was found that increased fluidization (lower bed densities) allowed for constant solid flows from the bed whereas decreased bed expansions (higher bed densities) lead to an intermittent flow. Particles would flow out of the bed as a dense slurry into the recycle line causing head pressure to build and shutting off the flow. Once the particles in the recycle line had emerged, head pressure would drop allowing more particles to enter the flowstream. This cycle would continue indefinitely at a frequency of several seconds.

The discharge of particles from the bottom of the bed did not appear to affect fluidization within the bed. No evidence was seen for poor fluidization on the deposits inside the bed near the discharge port. The flow of solution into the top of the bed, however, did appear to disrupt the fluidization with the top section of the bed. Care was needed to position the pipe inlet in such a way that the discharge did not aim directly into the bed but so solution flowed off the side wall of the expansion cone.

VII. ELECTROCHEMICAL EXPERIMENTS

The objectives of the electrochemical experiments were to: (a) define current-voltage relationships for the fluidized bed cell; (b) develop correlations between productivity and current density and degree of fluidization; (c) measure current efficiency as a function of copper concentration and; (d) determine energy required per unit of copper produced as verified by material balances. Two types of conducting particles were employed in the fluidized cathode: copper particles with a mean size of about 0.2 mm and graphite particles with a mean size of about 2 mm. Different operating strategies were used with each type of material. For copper, a truly fluidized bed was attempted with bed expansions of 20% or more. For the graphite particles, flow was controlled at the minimum fluidization velocity (bed expansions less than 5%) or the bed was maintained in a fixed state and periodically fluidized to break particle clusters.

In all cases, the electrolyte to the cell was a leaching solution from a small-scale industrial sulfuric acid leaching circuit. Sufficient electrolyte was taken from the leaching circuit for a number of electrowinning experiments. This solution contained copper at various concentrations ranging from about 10 to 30 gpl and sulfuric acid from about 60 to 90 gpl. (Acid concentrations were lower than those normally encountered in leach-electrowin circuits to inhibit the dissolution of copper into solution.) Electrolytes also contained significant concentrations of zinc ranging from 15 to 30 gpl along with minor amounts of nickel.

Temperature was allowed to vary during the experiments. Initially electrolytes were about 20° C and increased about 2° C per hour at 4000 amps and with sufficient flow to provide 20% bed expansion. The rate at which temperature rose depended on many factors with cell current being most significant followed by pumping rate and finally environmental conditions. (The contribution of pumping energy to overall temperature increase was measured to be about 0.5° C per hour.) At no point however did the solution temperature exceed 60° C. At this upper limit, heat losses from the system due to evaporation and convection equaled energy input to the system in the form of IR drop and pumping energy.

The strategy for these experiments was straightforward and similar to the one adopted in Phase II; operating variables were specified (extent of fluidization and current density in most cases) and an experiment was carried out until problems developed or until electrodes were removed for inspection. Current efficiencies were measured by changes in copper concentration and, at times, verified by material balance calculations. Problems that terminated an experiment included short-circuiting (the most common case, identified by high temperatures at some electrode connections and low voltage across the cell), poor current efficiency, hydrogen evolution at or near cathode current feeders, and equipment failure (generally loss of power to electrical equipment). At the end of an experiment, the cell was dismantled and the cause of the problem identified. Another set of variables, which could include changing the electrode spacing or bed height, was then selected for the next experiment. The variables examined in this manner were:

- particle size (coarse or fine)
- particle composition (copper or graphite)
- extent of fluidization (bed expansion)
- current density

As mentioned, variables associated with electrolyte (except for the use of additives for several experiments), including cell temperature, were not considered experimental variables. Two design variables, electrode spacing and membrane-to-anode spacing were also examined.

A. Deposition on Copper Particles

The original intent of this work was to evaluate the effectiveness of a fluidized bed of fine copper particles for the recovery of copper from sulfate electrolytes. Following our Phase II work, it was decided to use fine copper particles in the bed to promote smooth fluidization and avoid areas of high (or low) bed density that could lead to particle clusters and subsequent short-circuiting. It was recognized that fine particles, with their higher surface area, would be more susceptible to dissolution, but it was hoped that this could be overcome by keeping all particles in cathodic regions close to current feeders.

Table 6 summarizes experimental conditions and findings for the several experiments we conducted with copper particles. Experiment C-1, at a bed expansion of 20% and at 3800 amps, replicated the optimum operating conditions found in the Phase II investigation. (Note that the distributor plate with the 1 mm holes was used, resulting in a substantial pressure drop across the distributor plate and ensuring uniform flow.) Results from Experiment C-1 were comparable to those from Phase II: overall current efficiency was about 70% and, after a period of several hours, the bed had to be shut down because of short circuiting. Figure 17 presents a plot of copper concentration versus time for this experiment. As indicated, current efficiency was initially higher than 70% but dropped as time progressed.

More significant than the current efficiency, however, was the form of the deposition. As in Phase II, cathode current feeders were coated with a hard, dendritic deposit of copper. At certain points, particularly near the top of the fluidized zone, particles had collected around the dendrites into a cohesive mass that eventually short-circuited the cell. It was not clear how much deposition had occurred on particles, on current feeders or on particle clusters. What was obvious was that continuous operations could not be maintained.

The deposition encountered in Experiment C-1 led to the conclusion that excessive deposition was occurring on the current feeders at high current densities resulting in dendritic growth. These dendrites were responsible for poor fluidization in certain areas which in turn led to short-circuiting. This hypothesis was at odds with conclusions from the Phase II study; i.e., that areas of high bed density resulting from aggregative fluidization caused particle clustering and eventual short-circuiting.

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Table 6. Summary of Phase III Electrochemical Tests with Copper Particles.

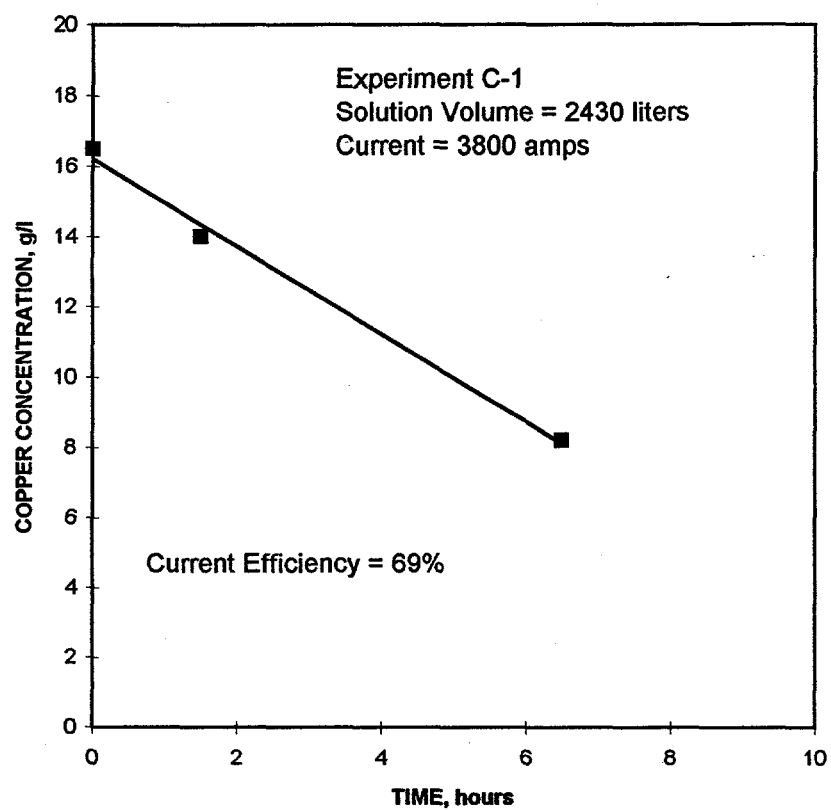| Test	Bed Expansion (%)	Duration (hr)	Current (amp)	Cell Voltage (volts)	Current Efficiency (%)	Comments
C-1	20	6.5	3600 - 4000	2 - 4	69	1 mm hole; 26 anodes; 70 cathodes
C-2	60	5	1950	4.5	< 0	2 mm hole; 15 anodes; 49 cathodes
C-3	60	5.5	4000	6	45	2 mm hole; 15 anodes; 49 cathodes
C-4	20	7	2000	3	< 0	2 mm hole; 14 anodes; 70 cathodes

Figure 17. Change in copper concentration with time for Experiment C-1.

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To test the new hypothesis, two experiments were run at high bed expansions where the degree of fluidization was known to be uniform and where particle spacing was such that a significant fraction of the overall current would be expended on deposition on the current feeders. Experiments C-2 and C-3 were both performed at bed expansions of 60% with Experiment C-2 at 2000 amps overall current and Experiment C-3 at 4000 amps. As expected, current efficiencies dropped substantially (net dissolution occurred in Experiment C-2) because the number of anode-cathode pairs was reduced in the cell. But current efficiency was not of interest in these experiments. The objective was to examine the nature of the deposit at the end of the experiments. In both cases, the deposit was similar to the one found in Experiment C-1 -- hard dendritic growths on current feeders, extremely difficult to remove, leading to eventual short-circuiting. Again the shorts were not a simple dendrite growing between an anode-cathode pair but a coherent growth of particles welded together by deposited copper and possibly resulting from a rough, horizontal surface on a current feeder.

A final experiment was performed with the fine particles (Experiment C-4) in which the degree of fluidization was again brought down to 20% and the current reduced to 2000 amps. In this case, the number of anodes was reduced as well although the entire contingent of cathode current feeders was present. Net current efficiency was negative because of the low current and again short-circuiting developed. Once again, short-circuiting developed because of dendritic growth from the cathode current feeders.

It was concluded that the cause of short-circuiting was not due to the type of fluidization (aggregative or smooth) but due to poor transfer of current into the mass of particles. Charge transfer could be improved by operating at lower bed expansions. But previous work clearly showed that 20% bed expansion was near optimal. The other option, and the one selected here, was to increase the size of the particles in the bed.

B. Deposition on Graphite Particles

Increasing the size of the particles in the bed offered at least four advantages. First, the flow required for fluidization would increase ensuring a satisfactory pressure drop across the distributor plate with the 2-mm hole size. Second, particles on the order of 1 mm are more typical of prior fluidized bed electrowinning investigations allowing comparisons to be drawn. Third, one can conjecture that large particles facilitate charge transfer into the bed compared with fine particles. The probability of simultaneous collisions forming a conductive chain of a given length is higher for large particles than for small particles. Finally, by selecting a conductive particle whose color contrasted with copper, it could be possible to visually observe areas in the bed where deposition was occurring. For all of these reasons, particles of conductive graphite were selected for testing.

When the graphite particles were first proposed for experimentation, the intent was to perform electrochemical experiments under the same basic conditions as had been used for copper

particles, i.e., at a fluidization of about 20%. However, examining the dendritic deposits formed from current feeders when using copper particles gave rise to the idea of a fixed bed of graphite particles with periodic pulsing to promote mixing. By shifting the area of deposition away from the current feeders towards the membranes covering the anodes, it was hoped to prevent deposition on current feeders. The question was: how quickly would deposition progress at the surface of the membrane?

To provide a rough answer to this question, a laboratory beaker was filled with graphite particles and electrolyte. A cylindrical mesh basket (about 3 cm in diameter) was inserted into the graphite particles into which was placed a titanium anode. The mesh basket prevented graphite particles from contacting the anode. After inserting a current feeder into the graphite, a current was applied across the cell (0.5 amps at 2.5 volts). Within 5 hours, essentially all copper was removed from solution at a current efficiency exceeding 70%. More importantly, it was observed that copper dendrites did not protrude through the plastic mesh separating the cathodic particles from the anodic electrode. Deposition, though not uniform, was distributed through the graphite mass from top to bottom and from front to back. This was accomplished without mixing of any kind.

With this result in hand, it was decided to attempt similar experiments at a larger scale. Graphite particles were charge to the fluidized bed reactor and after performing experiments to provide fluidization parameters (discussed in the previous chapter) electrochemical experiments began. As part of preliminary experiments, the effect of fluidization on the voltage drop through the cell was measured. Results are shown in Figure 18. Following expectations, increasing the extent of fluidization reduces the amount of current that can be passed at a given voltage drop; bed resistivity increases with bed expansion. Increasing bed expansion from 0% (a fixed bed) to 5% has a greater effect on bed resistivity than increasing bed expansion from 5% to 15%.

A summary of experimental conditions and results for the twenty or so electrochemical experiments performed with graphite particles is given in Table 7. Experiments can be divided into two types: low fluidization experiments at bed expansions less than 10% and fixed bed experiments with intermittent fluidization. Unlike experiments with copper particles, some experiments involved the use of additives to inhibit dendritic growth at current feeders. For these experiments, additions of hydrochloric acid, thiourea and glue were made on a continuous basis to cell electrolyte. (Solution containing 0.2 g/l thiourea, 1.1 g/l hide glue and 4.3 g/l hydrochloric acid was pumped into the storage tank at a rate of 0.0125 l/min. The total solution volume in the system during the experiment was about 2300 l.) Other variables included electrode spacing and the distance between the membrane and anode.

Two basic observations can be made concerning the experiments with graphite. First, deposition did occur on particles. The contrast between the black surface of unplated graphite particles and the red surface of freshly deposited copper clearly demonstrated that deposition took place. This did not occur uniformly through the bed on all particles; not all regions in the bed were electrochemically active and in the non-active regions no copper deposited. As experiments
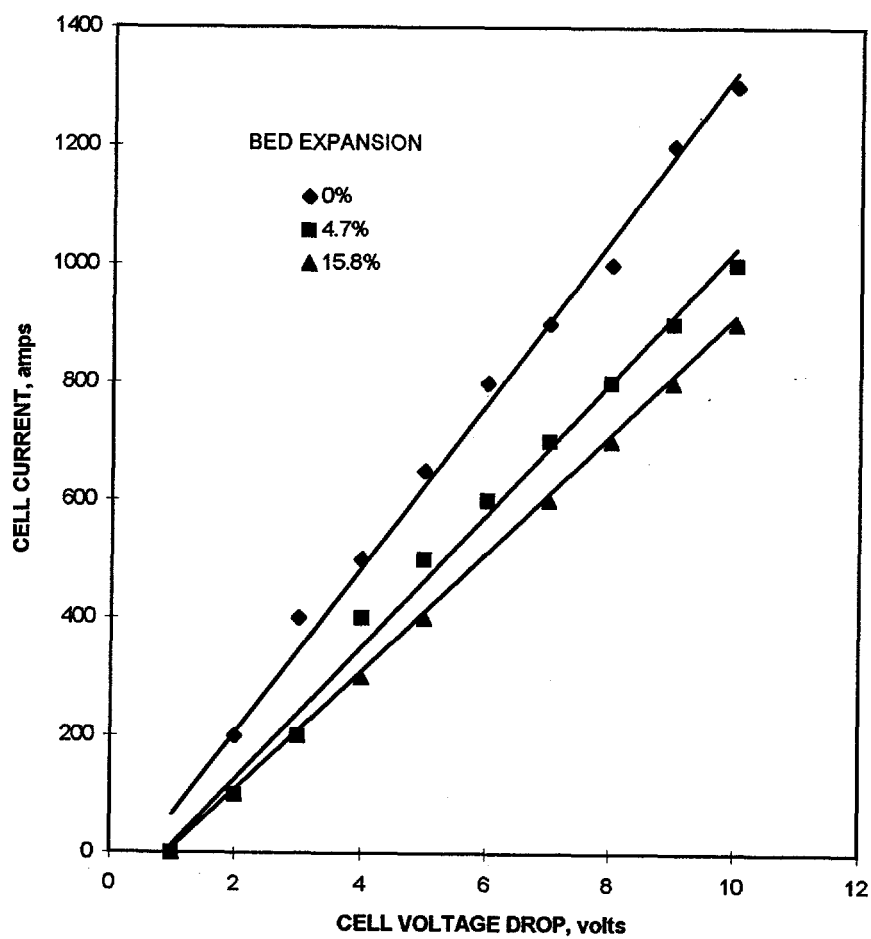
Figure 18. Relationship between cell current and voltage drop at various bed expansions.

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Table 7. Summary of Phase III Electrochemical Tests with Graphite Particles.

Experiment	Fluidization (%)	Duration (hr)	Current (amp)	Cell Voltage (volt)	Current Efficiency (%)	Comments
G-1						Initial test with graphite particles
G-2						Circulation of graphite particles
G-3		2.5	2000	5 to 1	20.5	Stopped due to shorting
G-4	7	5.5	700 to 1800	2.5	0.0	Used additives to smooth deposition on current feeders
G-5	minimum	3	1400 to 3800	2.5	73.1	Intermittent fluidization – 30 min low flow, 5 min 90 gpm
G-6	11	7.5	1200 to 3800	2.5	34.1	Short circuiting; disconnected anodes as test progressed
G-7	5	7.5	500 to 600	2.5	32.8	Intermittent fluidization; 5 min flow at 120 gpm
G-8	5	4	600 to 1400	2.5	68.2	Intermittent every hour
G-9	5	6.5	600 to 1300	5	15.7	
G-10a	5	3	600	5	-11.4	Intermittent every half hour
G-10b	5	5	600	5	0.0	
G-10c	5	9	800 to 900	5		
G-11	0	7.5	800 to 1000	5	61.4	Copper buildup on cathode rods; easily removed
G-12	0	7	600 to 1200	5	78.0	
G-13	0	7	800 to 2400	5	36.6	
G-14	0	15	1400	4 to 2.5	39.6	Copper buildup on membranes
G-15	0	4.5	1000	5 to 4	68.2	Increased spacing between membrane and anode; added copper-free anolyte; bubbles in cathode
G-16	minimum	7	1000	5	-5.8	Increased flowrate to prevent bubbling in cathode
G-17	5	15	1000	5.5	1.4	Anode solution copper increased from 3.5 gpl to 7.7 gpl
G-18	5	7	1000	5.5	-43.9	Bubbling in cathode; deposition on electrodes
G-19	10	4	1000	11	10.2	
G-20	0	5	1000	7 to 4.5	16.4	Heavy buildup of particles near anodes
G-21	0	5	1000	7 to 4.7		
G-22	0	7.5	1000	5.5 to 4.1		
G-23	0	5	1000	5.5		

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progressed, the bed would change from all black particles, to mostly black with a few red particles to mostly red particles. Second, most deposition appeared to take place next to or near anode membranes. Clusters of plated particles could be found near some cathode current feeders (particularly where a feeder was close to an anode surface due to improper alignment) but for the most part it was the anode surface that was coated with deposited copper particles when the cell was dismantled.

As with copper particles, experiments were usually curtailed because of short-circuiting. One or two anodes would begin to heat up and cell voltage would drop. Attempts were made to prolong experiments by disconnecting individual anodes (and this temporarily allowed experiments to continue at reasonable voltage drops) but eventually so many anodes would be disconnected that the experiment would be curtailed. Unlike experiments with copper particles, particle aggregates that collected around electrodes, whether anodes or cathode current feeders, were easily broken up and removed. The hard tenacious deposits on current feeders found in experiments with copper (in Phase II and III experiments) were not encountered. Additives could be partly responsible for this, but it is believed to be mostly due to fact that more current was transferred to the particles on whose surface deposition occurred.

Close examination of the electrodes at the end of most experiments revealed that some deposition occurred on the anode side of the membrane. In fact, most membranes contained a multitude of microscopic dendrites passing through their surface connecting them to the anode. It was as if membranes had been welded to the anode surface. Several remedies were attempted to prevent this phenomenon from occurring. Under the assumption that sufficient mixing was not taking place near anodes, the spacing between anodes and cathodes was dramatically increased. Changing this spacing could not be done in small increments because of the design of the electrode supports and busbar system. What was done instead was to surround an inner ring of anodes with a few cathode current feeders as shown in Figure 19. This effectively increased spacing by a factor of four. The wider spacing, it was felt, would allow the surfaces of the anodes to be effectively "cleaned" during intermittent periods of fluidization. However, this did not prevent the buildup of deposits around the anodes. Next, the spacing between the anodes and the membrane was increased by installing polypropylene mesh on the anodes installing membrane. Initially, membranes were placed directly on the anode surface, following the practice of the Berkeley team, to minimize voltage drop. The polypropylene mesh allowed a gap of about 3 mm between membrane and anode. This was doubled to 6 mm in later experiments, still without success. Anodes were also filled with solutions devoid of dissolved copper to prevent plating inside the membrane. Here mixtures of sulfuric acid and water were used. But, since the deposition occurred from the outside in, this was not effective in preventing eventual short circuiting.

In comparing the small-scale laboratory experiment with the larger experiments using graphite, it can be conjectured that the cause of the problem may have been the membrane itself. The membrane, consisting of many small voids surrounded by polypropylene, allowed adhesion of

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RING OF SIX ANODES

CATHODE BUS

RING OF
TWELVE CATHODE
CURRENT FEEDERS

ANODE BUS
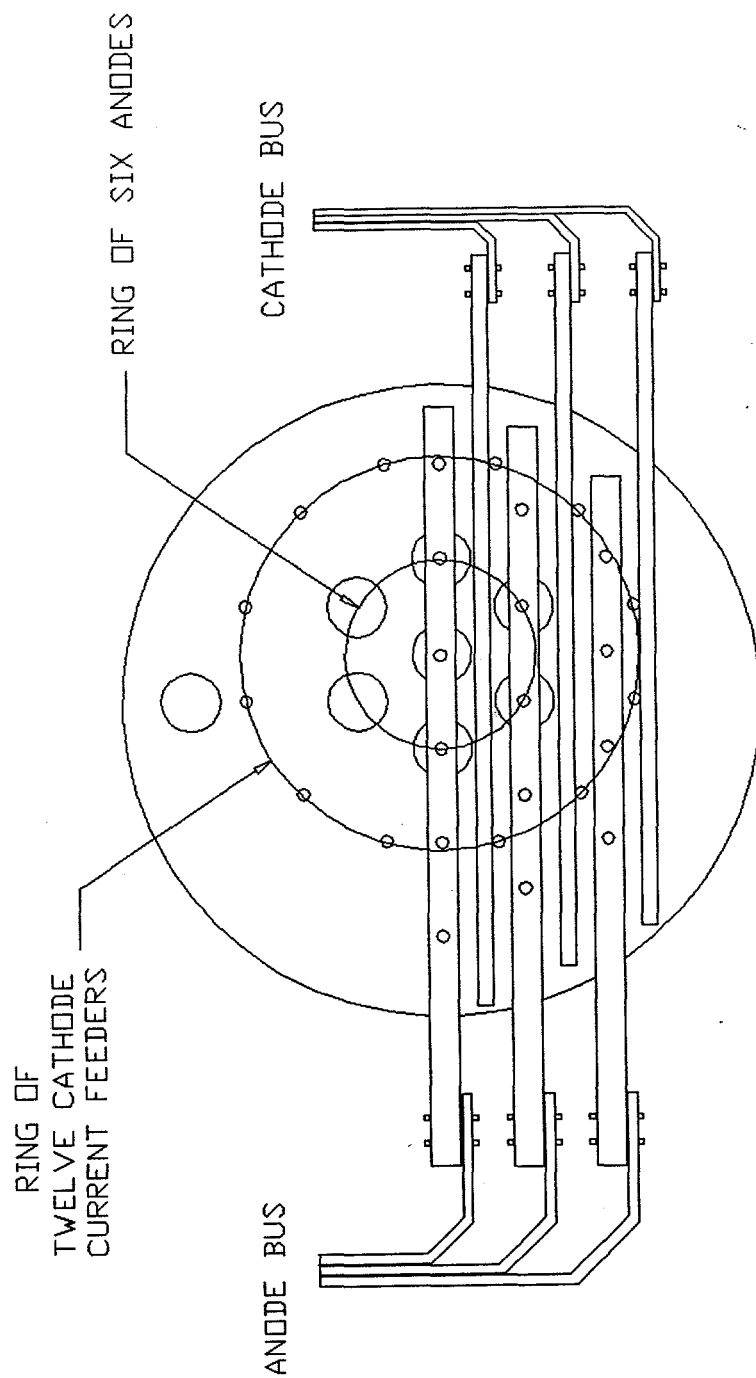
Figure 19. Electrode arrangement for wide-spacing experiments.

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small dendrites of copper. In the laboratory, no membrane was used; a simple mesh separated cathodic particles from the anode region. Any growths that might have formed through the mesh (though dendrites were not observed, perhaps because a sharp voltage drop did not occur across the mesh) could be easily removed. In contrast, the membrane could not be cleared of deposited copper because of the large number of tightly held, though microscopically small, dendrites. An alternative to eliminating the membrane (which besides keeping particles away from anodes, acts as a pressure drop to prevent solution from passing through the hollow anodes rather than the bed of particles) would be to install a mesh on the particle-side of the membrane thus preventing direct contact between particles and membrane. Further experiments to explore this possibility should be considered.

VIII. CONCLUSIONS AND SUGGESTIONS FOR FUTURE TESTING

This investigation examined the use of a fluidized bed electrowinning cell for the recovery of copper from sulfuric acid electrolytes. A pilot-scale fluidized bed unit having an electrochemical working area of about 1 m high by 1 m in diameter was designed and constructed. A means was provided for the continuous recovery of coarse particles from the bed by circulating particles out of the bottom of the bed (using an eductor) past a size separation device; coarse particles could be recovered and fine particles returned to the top of the bed for further deposition. Materials handling experiments showed the system for circulating particles out of the bed was workable.

Two types of electrochemical experiments were performed. In the first series of experiments, the cathode consisted of a fluidized bed of copper particles with a mean diameter of 0.2 mm. Under a variety of fluidization conditions and with various electrode spacings, a set of operating conditions could not be found in which short-circuiting did not eventually occur. Examination of the short-circuiting deposit revealed that copper dendrites formed on the cathodic current feeders and interfered with fluidization; in these regions, particles clustered together, became attached to current feeders and eventually formed a short circuit. Current efficiencies ranged from about 70% for these experiments to less than zero (net dissolution). But current efficiency should not be used as the measure of success for these experiments; copper deposition occurred at the wrong place to allow long-term operation. Conditions that favored good fluidization (wide electrode spacing, low bed densities, fine particles) promoted dissolution while conditions that minimized dissolution promoted short-circuiting.

In a second series of experiments, significantly larger graphite particles (with a mean size of about 2 mm) were used as the fluidized media. The objective of these experiments was to maintain good contact between particles and the cathodic current feeders so as to promote deposition on the particles. The bed was therefore maintained at or near minimum fluidization. Periodically, intense fluidization was applied to breakup particle agglomerates formed during the deposition cycle and clean off the surface of the membrane separating anodes from the cathodic reaction. Under these conditions, deposition occurred near the membrane and eventually numerous small dendrites of copper would pierce the separator and short-circuit the cell. Again, a set of conditions could not be found that would allow long-term operation at reasonable current efficiencies.

It was concluded that fluidized bed electrowinning, under the set of conditions investigated here, is not a viable approach for the recovery of copper from sulfuric acid electrolytes. Of the two modes of operation, a stagnant or barely fluidized bed periodically pulsed to mix particles appeared to be the most promising for long-term operation but requires further research to optimize frequency of pulsation. Improved separators with smooth impregnable surfaces to prevent attachment of microdendrites would be necessary.

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However, this is not to say that particulate electrodes in general and fluidized bed electrodes in particular are not appropriate for all electrochemical systems. Fluidized beds seem to be ideally suited to systems in which little or no deposition occurs. In such systems, good particle contact could be maintained without the need to constantly mix the bed to prevent clustering and short-circuiting. Possibilities include:

- Cathodic reactions in which only small amount of deposition occurs as in the treatment of wastewater solutions for the recovery of trace metals or the oxidation of certain constituents of wastewater into less toxic forms, for example in the detoxification of cyanide-containing wastewater.

- Anodic reactions in which a soluble species is oxidized to another soluble species as in the oxidation of Fe^{+2} to Fe^{+3}.

Finally it is important to note that there exist devices similar to fluidized bed cells that offer many of the advantages but apparently without the disadvantages (or more properly put, with a different set of disadvantages). In this category are spouted bed reactors[28,29] that have recently been receiving attention and pulsed bed cells, now on the market for metal recovery from wastewater.[30] These units operate on the principal of maintaining close particle proximity during deposition cycles, allowing charge to be effectively transferred from cathodic current feeders into the mass of particles. It is in this direction that future research with fluidized bed electrodes must be aimed if long-term operations are ever to be achieved.

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APPENDIX A

EXPERIMENTAL PLAN

EXPERIMENTAL PLAN:

FLUIDIZED BED ELECTROWINNING OF COPPER

COOPERATIVE AGREEMENT NO. DE-FC07-921D13081

Submitted to:

U.S. Dept. of Energy
Contracts Management Division
Idaho Operations Office
Idaho Falls, Idaho 83402

David Robertson
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Submitted by:

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David J. Kinneberg
Project Leader

February 16, 1995

I. PURPOSE AND SCOPE

This document presents the experimental plan to demonstrate the technical feasibility of fluidized bed electrowinning of copper in a 10,000-amp experimental cell. This plan is divided into two parts: materials-handling tests and electrochemical tests. For each part, the overall objectives of the test are presented followed by detailed descriptions of individual experiments.

Attached to this document as appendices are the standard operating procedures for this system and a description of the safety interlocks.

II. DESCRIPTION OF EXPERIMENTAL SYSTEM

Figure 1 presents an engineering diagram of the 10,000-amp fluidized bed electrowinning cell designed and constructed for these tests. The cell is fabricated in three sections of polypropylene wrapped with Fiberglas. The unit itself can be divided into three functional volumes. Solutions containing soluble copper are pumped into the lowest section, the feed plenum, to equalize pressures across the distributor plate. From there. solution flows across the distributor into the working volume of the cell. It is in this region that copper deposits on a fluidized mass of cathodic particles while oxygen is produced on cylindrical anodes (not shown). Above the working volume of the fluidized bed is a disengagement zone, where the solution velocity drops below that necessary to fluidize particles, thereby preventing solids from leaving the bed.

Figure 2 gives the piping and instrumentation diagram (P&ID) for the installation showing the interconnections between the various pieces of equipment. The three flow streams into the fluidized bed from Tank T-751 are of particular interest. Pump P-752 provides the fluidizing flow stream into the feed plenum at the bottom of the reactor. Pump 753 provides anolyte into the 26 anodes suspended into the reactor's working volume. Pump 751 provides a flow stream to circulate solid particles, falling out of the bed at a controlled rate, up to the top of the installation where they can be retained for future screening in Tank T-752 or be returned to the cell.

Figure 3 gives a overview of the actual layout of equipment showing the actual physical relationship between the rectifier, control panel, tanks and pumps.

III. MATERIALS HANDLING TESTS

A. Objective: To insure that :
- all equipment has been properly fabricated and installed and is leak-proof;
- the electrodes can be withdrawn for easy inspection and the reactor disassembled when needed;
- operating procedures are satisfactory for starting and stopping fluidization (including filling the bed with particles and emptying the bed at the end of a test);
- particles can be circulated through the recycle loop and that particle size separations can be performed;
- an excessive amount of particles do not "leak' through the distributor plate_when the bed is not fluidized; and
- operators are familiar with emergency procedures.

B. Experiment Descriptions:

1. Static Water Tests

With all nozzles and other openings sealed, the fluidized bed, Tank T-751 and Tank T-752 will be filled to their operating capacities with water four a period of 24 hours. If no leaks are observed, the test is successful. If not, manufacturers will be contacted and adjustments/repairs made until the experiment can be successfully performed.

2. Dynamic Water Test

Using water, the fluidized bed system will be operated for a period of 4 hours while watching for leaks. During this period, the fluidization pumps, circulation pump and anode feed pump will be operated at 100% of design flowrates. Pressure drops will be recorded as a function of flow rate for the distributor, and pump outlets to serve as bench marks in future tests. Solution will periodically be diverted to Tank T-752 to check for structural integrity. At least twice during this test, the Emergency Shutdown button will be activated to see if all equipment shuts off as expected and that the system can be restarted.

3. Dynamic Slurry Test

Again using water, copper shot will be added to the fluidized bed and the bed operated in a fluidized mode for a period of 4 hours. As in Experiment 2, the Emergency Shutdown button will be pushed at least twice during this period to allow particles to settle out. The system will then be restarted to see if the static bed can be fluidized In Situ. At the end of the experiment, half of the particles will be emptied from the reactor using the standard procedure via tank T-752 while half will be removed through the Emergency Discharge port. The electrodes will be removed from the unit and inspected. The lower portion of the feed plenum will be dismantled and any particles which "leaked" through the distributor plate will be collected and measured. The distributor plate will be inspected for clogs.

4. Connection with Existing Electrochemical Circuit

Water will be drained from the circuit and the piping connection with the existing electrowinning tank will be opened causing Tank T-751 to be filled with acidic copper sulfate solution to a predetermined level. The control system should maintain this level while continuously pumping solution between the two circuits for a period of 24 hours.

IV. ELECTROCHEMICAL TESTS

A. Objective: To measure critical operating parameters for the 10,000-amp cell at various operating conditions. These include:

- the current/voltage relationship at various degrees of fluidization;
- current efficiencies at various degrees of fluidization and superficial current densities; and
- location of copper deposition (fluidized particles or current feeders).

Series 5. Current-Voltage Relationship

Standard operating conditions will be followed to start-up the fluidized bed cell. Samples of the solution will be taken and electrolyte temperature noted. The rectifier will be turned on, and a scan performed through the range of rectifier outputs noting the current at various voltage levels. (The overall voltage drop measured at the rectifier will be recorded along with the voltage drop across the electrolytic cell.) After one hour, another solution sample will be taken, temperatures noted and the current/voltage scan repeated. The degree of fluidization will then be changed and the aforementioned procedure repeated.

Measurements will be taken at three levels of fluidization: 15%, 20% and 25%.

Series 6: Current Efficiency Measurements

These experiments consist of three 24-hour operating periods in which current efficiencies are measured as a function of degree of fluidization and superficial current density. Each 24-hour period will correspond to one level of fluidization and during that period three current levels will be investigated, each for an 8-hour period. A total of nine experiments are therefore planned, three different current densities (5000 amp, 7500 amp and 10000 amp) at each of three levels of fluidization (15%, 20% and 25%).

For each experiment, standard operating conditions will be followed to startup the fluidized bed reactor. The fluidized bed height will be adjusted to give level of interest for the experiment and the voltage set to provide the required current. For 8-hours the reactor will be held at these conditions. Every other hour, the flow between the two electrowinning circuits a will be stopped, simplifying a material balance around the fluidized bed. For a one-hour period, solution samples will be taken at 10-minute intervals. After six samples have been taken, solution flow between the circuits will be restarted allowing the fluidized bed system to recover from the perturbation. The copper content of the six solution samples will be measured using a DCP spectrophotometer. These values will be plotted as a function of time and the least-squares slope will be used, along with the known system volume and current flow, to compute current efficiency. After 8 hours, the current to the cell will be increased and four measurements of current efficiency will be taken in the same way. The entire sequence will be repeated once again at the third level of current density.

At the end of the experiment, the system will be shut down and the electrodes will be removed from the cell. Cathode current feeders will be inspected for deposits. The mass of particles from the bed will be screened to remove large particles in preparation for the next series of experiments at a different level of fluidization.

APPENDIX B

OPERATING PROCEDURES

METALOR USA REFINING CORPORATION
MEMORANDUM

DATE: January 5, 1994

TO: J.W. Evans (UC-Berkeley)   T. Oldham
           M.B. Mooiman   J.K. O'Neill
           R.M. Nadkarni

FROM: Dave Kinneberg

SUBJECT: Fluidized Bed Operations

PROJECT: 4046 (4046-4.mem)

This memorandum presents operating procedures for the fluidized bed electrowinning system. Equipment numbers refer to the attached Piping and Instrumentation Diagram. The following operation steps are described:

1. Startup
2. Routine Operation
3. Shutdown
4. Emergency Shutdown
5. Product Rinse

I. STARTUP

Assume the system is devoid of solution and solids.

1. Input 50% into the level control dial for tank T-751 and push the start button. (See DJK memo of 1/11/94 for a description of the level control system for tank T-751.) Allow the tank to fill to this point.

2. Using the barrel dumper, pour 1/4 drum of copper particles (1000 lbs) into tank T-752 in preparation for addition to the FBE reactor. The weight of particles in the drum must be known. Valve V-765 must be closed.

3. Start pump P-752 (fluidization pump). Adjust the flow control valve to obtain a flow of 250 gpm. Allow sufficient time for the FBE reactor to fill and begin overflowing back into tank T-751.

4. Set AV-753 to divert particles into FBE reactor. By opening valve V-765, slowly add copper particles to the fluidized bed. Do not add them so quickly that the bed sloshes over. Close valve V-765 when tank T-752 is empty.

5. Add another quarter drum of copper particles to tank T-752. Empty particles into FBE as in step 4. Repeat these steps two more times (for a total of 4000 lbs)

until the particle level in the FBE is at the appropriate height for the experiment. (The relationship between degree of fluidization and flowrate will be determined in preliminary fluid flow tests. We will be able to compute the bed height for a given mass of particles and flowrate and compare this against the measured value in the reactor.)

6. Using the overhead hoist, insert the electrode assembly into the FBE body. Particle level will increase in the bed. Connect anode and cathode feeders to bus bar. Attach the vent line to the reactor and reconnect the anolyte flow line and solid recycle line.

7. Start pump P-751 (solids recycle pump). Adjust the flow control valve FCV-753 to obtain a flow of 15 gpm.

8. Start pump P-753 (anolyte pump). Adjust the flow control valve FCV-751 to obtain a flow of 30 gpm.

9. Turn on the rectifier and using the control dials, set amperage to desired level for the experiment at hand.

10. When appropriate, open valve V-764 to allow particles to discharge from the FBE and be recycled.

II. ROUTINE OPERATION

With the exception of recording process variables (temperature, current, voltage), there are no specific duties requiring an operator for routine operations. In this respect, the fluidized bed system is similar to the present copper sulfate cells.

However, because this is an experimental system, there will be certain observations and/or measurements that must be made. Two of the most crucial will be checking for copper deposition copper on current feeders and the measurement of current efficiency. The procedure for each of these measurements is given below.

A. Current Feeder Check

1. Shut off rectifier.

2. Close valve V-764 to stop particles from being recycled. After a period of two minutes, shut off pump P-751 (solids recycle pump).

3. Stop pump P-753 (anolyte pump).

4. Disconnect the vent line, the anolyte flow line and the solids recycle line from the electrode assembly. Disconnect anodic and cathodic current feeders.

5. Raise the electrode assembly and position it over the

mezzanine drip pan.

6. Put a light over the top of the electrode assembly and
    by looking from the bottom up, inspect all cathode
    current feeders for accretions. Check anodes for leak-
    ing membranes and/or deposition.

7. After the visual check, replace electrode assembly in
    FBE. Reconnect lines, turn on pumps and open valve V-
    764. Restart rectifier.

B. Current Efficiency Measurement

1. Stop the flow of fresh solution into tank T-751 by
    pushing the appropriate button on the panel board. Note
    the volume in the tank, bed height and fluidization
    flow. (Retention volume for the bed and pipe lines will
    be measured during preliminary tests.)

2. At ten-minute intervals over the next hour, withdraw
    solution samples from tank T-751. Note the time the
    sample was taken and the temperature and current of the
    FBE.

3. Current efficiency is determined from the slope of the
    least-squares line through the data points given the
    system volume and current flow.

III. ROUTINE SHUTDOWN

Electrolytic experiments should last anywhere from 2 to 8 shifts
depending on the objective of the particular test. At the end of
the test, particles must be removed from the bed while the bed is
fluidized to prevent particle leakage through the distributor
plate.

There are two methods for removing particles from the bed. The
first method is to empty the bed directly into 55-gal drums via
valve V-763. The second is via tank T-752. Instructions for
both are given below.

A. Emptying FBE via Valve V-763

This method has the advantage of speed but results in a high
liquid inventory in 55-gal drums. It is not possible to rinse or
size particles using this method (unlike method B below).

1. Shut off rectifier.

2. Shut valve V-764 to stop the flow of particles out of
    the FBE reactor. After two minutes, stop the solids
    recycle flow (pump P-751).

3. Stop anolyte flow (pump P-753).

4. Open Valve V-763 and close V-762.

5. Slowly open Valve V-764, allowing particles to flow out of the FBE reactor and into a drum on the ground floor. When the drum is 1/3 to 1/2 full, switch to a new drum. Continue filling drums until no further particles are seen to be exiting the bed (four or five drums depending on the volume of solution.

6. Stop the fluidization pump P-752 and close valves V-764 and V-760 to prevent the bed from draining.

7. If necessary, remove electrode assembly for inspection.

B. Emptying FBE via Tank T-752

1. Shut off rectifier.

2. Manually override computer control of AV-752 forcing flow into tank T-752 instead of the FBE. Fill tank T-752 with particles until the high level for solids is reached.

3. Switch AV-752 so that flow resumes to FBE reactor. If rinsing is required, follow instructions given in section V below.

4. If required, position screen in flow stream. Empty Tank T-752 into drums using V-765 and AV-753. If required, insert screen into flow stream and separate particles by size. Fill drums no more than half full.

4. Repeat step 3 until FBE reactor is devoid of particles.

IV. EMERGENCY SHUTDOWN

The emergency shutdown sequence can be initiated by the operator as needed or by the computer if the FBE is overflowing. The following events then take place:

1. The rectifier shuts off.

2. Pumps P-751, P-752, P-753 and P-754 shut off.

3. Air valves AV-751, AV-753 and AV-754 close. All other valves remain in the present state.

Particles will settle to the distributor in the FBE and in the discharge line above V-763. However, there will be no back flow through the distributor because of the automatic action of AV-754 and AV-755.

Startup from an emergency shutdown is as follows:

1. Find the cause of the shutdown and make appropriate changes.

2. Close Valves V-760 and V-764.

3. An ESD bit within the PLC must be reset by an engineer. This will release air valves AV-751, AV-753 and AV-754 to open.

4. Initiate flow into tank T-751 from T-702 by pressing the start button on the panel.

5. Start the fluidization pump P-752 and slowly open valve V-760. Flow should increase to its value prior to shutdown.

6. Start anolyte pump P-753 and solids-recycle pump P-751. Slowly valve V-764 begin recycling solids.

If the distributor has been clogged by solids, it may be necessary to empty the bed manually from the top. (This was never required during Phase II even with a much cruder solution flow scheme.) Before attempting a manual cleanout though, two other options must be first attempted: high-pressure plant water via valve V-568 or acid wash/soak with solution from tank T-751.

V. PRODUCT RINSE

It is necessary to rinse excessive solution off the surface of copper particles before drying. This is accomplished in tank T-752.

1. With particles in tank T-752 (vale 765 closed), open valve V-766 allowing solution to drain into tank T-751. (A filter element will be inserted into the line upstream of valve V-766 to prevent particles from emptying from the tank.) When tank is empty, close valve V-766.

2. Open valve V-767 and fill tank T-752 with city water. After a ten-minute soak, empty the tank as per step 1.

3. Repeat as many times as been determined to be necessary during preliminary tests.

METALOR USA REFINING CORP.

FLUIDIZED BED ELECTROWINNING
DRAWING No. 4046-1
PIPING & INSTRUMENTATION DIAGRAM

REV.	DATE	INIT.	DESCRIPTION
B	1/10/94	DJK	FOR HAZ-OP REVIEW
A	12/15/93	DJK	FOR IN-HOUSE REVIEW